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Variational theory of average-atom and superconfigurations in quantum plasmas

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Models of screened ions in equilibrium plasmas with all quantum electrons are important in opacity and equation of state calculations. Although such models have to be derived from variational principles, up to now existing models have not been fully variational. In this paper a fully variational theory respecting virial theorem is proposed—all variables are variational except the parameters defining the equilibrium, i.e., the temperature T, the ion density n_i and the atomic number Z. The theory is applied to the quasiclassical Thomas-Fermi (TF) atom, the quantum average atom (QAA), and the superconfigurations (SC) in plasmas. Both the self-consistent-field (SCF) equations for the electronic structure and the condition for the mean ionization Z^* are found from minimization of a thermodynamic potential. This potential is constructed using the cluster expansion of the plasma free energy from which the zero and the first-order terms are retained. In the zero order the free energy per ion is that of the quantum homogeneous plasma of an unknown free-electron density $n_0=Z^* n_i$ occupying the volume $1/n_i$. In the first order, ions submerged in this plasma are considered and local neutrality is assumed. These ions are considered in the infinite space without imposing the neutrality of the Wigner-Seitz (WS) cell. As in the Inferno model, a central cavity of a radius R is introduced, however, the value of R is unknown *a priori*. The charge density due to noncentral ions is zero inside the cavity and equals en_0 outside. The first-order contribution to free energy per ion is the difference between the free energy of the system "central ion+infinite plasma" and the free energy of the system "infinite plasma." An important part of the approach is an "ionization model" (IM), which is a relation between the mean ionization charge Z^* and the first-order structure variables. Both the IM and the local neutrality are respected in the minimization procedure. The correct IM in the TF case is found to be $Z-Z^*=\int d^3r[n(\vec{r})-n_0]$, where $n(\vec{r})$ is the first-order electron density. It is shown that in the QAA case the same IM has to be used and that other IMs lead to unphysical solutions. With this IM R becomes in both cases (TF and QAA) equal to the WS radius and the variational calculation leads to SCF equations in an infinite plasma while n_0 (or equivalently Z^*) is to be found from the condition $\int d^3r\, \theta(r-R)V_{el}(\vec{r})=0$, where θ denotes Heaviside function and $V_{el}(\vec{r})$ is the SCF electrostatic potential. In the SC case results are similar except that averages over all superconfigurations appear. In the TF case the condition for n_0 gives the neutrality of the WS sphere and one gets the classical TF ion-in-cell average atom. The situation is different in the QAA and in the SC cases in which the cavity is not neutral and the SCF potential $V_{el}(\vec{r})$ is not zero outside the cavity. Due to the fully variational character of our approach the expression for the thermodynamic pressure in all cases does not require any numerical differentiation and is consistent with the virial theorem.

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I. INTRODUCTION

Models of atoms or ions in plasmas are of interest for inertial fusion, for astrophysical plasmas, and for laboratory hot dense plasmas. This remark especially concerns plasmas in which part of the electrons remains bound to the ions. This is practically always the case in plasmas containing medium or high Z elements. As is well known, medium Z atoms like iron still have bound electrons even at conditions corresponding to plasmas at the center of the Sun. The importance of bound electrons results from their dominant role in photoabsorption and the emission of radiation in plasmas. In such a way bound electrons are also responsible for the dominant radiative energy transfer in hot dense plasmas.

The aim of the paper is to formulate fully variational models of quantum average atom (see, for instance, Refs. [1–3]) and superconfigurations [4–6] in plasmas at finite temperature. Such models are needed in order to correctly treat plasma thermodynamics. This is important for plasma equation of state (EOS) and also for other applications such as plasma opacity calculations.

The first approach to the atom in the plasma problem was based on the finite temperature Thomas-Fermi (TF) model [1]. This TF model in which the atom was confined in the Wigner-Seitz (WS) sphere (ion-cell model) was inspired in large part by models used in solid-state physics [2]. The TF model of Ref. [1] yields a consistent EOS, i.e., a simple expression for the thermodynamic pressure due to electrons. As shown in Ref. [1] the TF model respects exactly the virial theorem. This is connected to the fully variational character of the model and to its correct scaling properties [1]. The equilibrium is uniquely determined by three parameters of the plasma: the matter (ion) density n_i, the temperature T, and the atomic number of plasma atoms, Z. The ion density is related simply to the WS radius by the relation $R_{WS}=[3/(4\pi n_i)]^{1/3}$.

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A first comprehensive quantum extension of the average atom was the model proposed by Rozsnayi [3]. In the self-consistent-field (SCF) calculation presented in Ref. [3] bound electrons are treated quantum mechanically, i.e., via the Schrödinger equation while the free electrons are still quasiclassical, i.e., described as a TF fluid. The problem with Ref. [3] is that that model is not supported by a variational derivation. Moreover, the TF approach to free electrons in Ref. [3] cannot lead to the correct treatment of pressure ionization [7,8] that occurs when bound states disappear and are compensated by resonances in the continuum. Such resonances have to be found from a SCF calculation with quantum free electrons.

First variational derivation of a relativistic SCF average atom model with quantum bound and free electrons was proposed by Liberman [9,10]. Liberman's model has been implemented in the Inferno code. The code has been the object of many improvements (see, for instance, Ref. [11], and references therein). In Liberman's model the bound and free electrons are considered in the whole infinite space. There are two main assumptions in Liberman's model: one is the required neutrality of the WS sphere and the second is the treatment of this sphere as a cavity, which means that outside the WS sphere there is a constant positive charge density of the value corresponding to the asymptotic negative electron charge density. Inside the WS sphere this positive charge of the noncentral ions is absent. Similarly, as in the TF model of Ref. [1], the neutrality of the WS sphere provides the value of the chemical potential and consequently, the value of the asymptotic electron charge density equal to the constant positive charge density. In Liberman's model the pressure is calculated from the derivative of the free energy of the finite part of the plasma contained in the WS sphere. That leads to problems with the virial theorem; some of these problems are related to the fact that wave functions always extend beyond any finite system. In practice the pressure in the Inferno code is calculated from a numerical derivative of the ion-cell free energy [11].

Perrot proposed to consider the average atom in the whole space also in the presence of the WS cavity [12]. In the AJCI model and in the code based on that approach the neutrality of the WS sphere is not required—Perrot shows in fact that the requirement of the neutrality of the WS sphere is not compatible with the variational principle. Instead, the neutrality of all the charges is imposed in the whole space. However, this last condition becomes identical with the requirement of the locality of the SCF potential and does not determine the chemical potential that is needed in order to provide the value of the asymptotic electron charge density. For that reason in the AJCI model a supplementary external condition is required in order to obtain the value of that asymptotic density. Without that supplementary condition Perrot's approach can be viewed as a fully variational model of an equilibrium characterized not by three but by four parameters: the matter density n_i, the temperature T, the atomic number of plasma atoms Z, and the asymptotic electron density n_0, where $n_0 = Z^* n_i$ and Z^* is an assumed known number of free (ionized) electrons per ion. In order to calculate the electronic pressure the AJCI model needs a function (external to the model) $Z^*(R_{WS})$, i.e., the number of free electrons per ion in the function of the average ion radius (or volume). That dependence in the AJCI model is taken from the TF model. Since with the exception of this external condition, the model is fully variational, the only numerical derivative needed to calculate the electronic pressure comes from the dependence $Z^*(R_{WS})$ [in practice the AJCI code uses the derivative $dZ^*(R_{WS})/dR_{WS}$ in the analytical approximate form proposed by More [13]].

In the present paper we propose a correct variational approach to the average atoms and superconfigurations in plasmas. The main new idea is to use the cluster expansion of the free energy of atoms in plasmas and to take into account the two first terms of this expansion. We try in this way to avoid problems present in Liberman's [9,10] and Perrot's [12] approaches. In both these approaches it appears necessary to use an external condition, which can provide the chemical potential, or equivalently, the asymptotic electron density n_0. As mentioned above in Refs. [9,10] this condition is taken in the form of the neutrality of the WS sphere, while in Ref. [12] it is taken in form of an external dependence $Z^*(R_{WS})$. In our opinion, the introduction of these external conditions (after the SCF equations have been obtained from a minimization of the free energy) makes that the models from Refs. [9,10,12] cannot be considered as totally variational. From the technical point of view we believe that the nonvariational character of Liberman's and Perrot's approaches stems from the fact that these authors have minimized only the first-order free-energy term in the cluster expansion and have not taken into account before the minimization procedure a correct ionization model. In our approach this ionization model leads to a dependence of the zero-order term on the variables of the first-order term. This allows us to minimize the total free energy (the sum of the zero- and the first-order terms).

The plan of the present paper is as follows. In Sec. II we will propose the general expression of the free-energy functional retaining only two first terms from the cluster expansion. The zero-order term of the free-energy functional is that corresponding to a homogeneous electron gas neutralized by a homogeneous constant density ion background. The expressions of the zero-order quantities will be given in Sec. III. As concerns the first-order functional we will consider in this paper three models of plasma atoms: the TF case (Sec. IV), the quantum average atom case (QAA) (Sec. V), and the superconfiguration case (SCs) (Sec. VI). In all cases we will retain the concept of the cavity but will consider the radius of the cavity as an independent variable not connected (at least from the beginning) to the WS radius. The prescription to construct the first-order contribution to the free-energy functional will be the same in the three cases. We assume that around a chosen central ion there will be a localized change in the electron density resulting in the appearance of a localized potential. As already proposed in Refs. [9,10,12] the first-order free energy will be equal to the difference between the free energy of an infinite system containing the central ion and the free energy of the homogeneous infinite system. The minimization will be performed with two additional conditions: the first is the general neutrality condition assuring the localized nature of the potential and the second the mentioned ionization model. In the superconfiguration case there will be other conditions corresponding to the definitions of the supershells [4–6]. The minimization will be performed with respect to all independent variables. Thus the thermodynamic pressure formula will be in a simple form that does not require any numerical differentiation. Section VII contains the main conclusions.

In order to guide the reader the main ideas of the paper can be presented with the help of references to the Inferno model [9,10], which is well known in the dense plasma community. As stated before in the Inferno model, one minimizes the difference of the free energy due to the presence of the central ion. In our approach this difference appears also but as the first-order term [we recall that the free-energy expression in our approach is the sum of the zero- and first-order terms (see Sec. II)]. The construction of this first-order term in the present paper and in the Inferno model is similar: the free energy is that of an ideal electron gas in the field of a SCF potential with a local density correction for the exchange and correlation in the quantum cases. As in the Inferno model in our QAA and SC cases the bound and free wave functions are normalized in the whole space (let us mention however, that the Inferno model is relativistic while the quantum models of this paper are nonrelativistic although their extensions to relativistic formalism are straightforward). The zero-order term that is present in our approach and that is absent in the Inferno model is the free energy of a homogeneous electron gas occupying the volume of one ion that is equal to $1/n_i$, i.e., the inverse of the ion density (see Sec. III). The presence of the zero-order term stems from the cluster expansion used in our approach. It can be easily understood from the physical point of view since the first-order term contains only a part of the free energy that is bound to the ion and not the free energy of the plasma electrons that remain unbound (bulk plasma electrons). When electrons are ionized both the zero-order and the first-order free-energy terms are affected by this process (the ionized electron leaves the "bound" population and appears in the bulk of the plasma) and for that reason the right expression to be minimized is the sum of both terms. Contrary to the Inferno model in the present paper the notion of the ion cell and its geometrical volume is not used: the ion volume $1/n_i$ is introduced only to calculate zero-order quantities, i.e., those of the homogeneous electron gas. Due to the fully variational character of our approach, the thermodynamic pressure can be expressed by the explicit derivative of the thermodynamic potential with respect to the ion density (the meaning of the explicit derivative is given in Sec. II and Appendix A). In the Inferno model a cavity of the WS radius is introduced and the neutrality of the WS sphere is imposed. The WS sphere neutrality in the Inferno model allows one to calculate the chemical potential, or equivalently, the average free-electron density n_0, which in the Inferno model is equal to the electron density at the WS radius. Moreover, in the Inferno model the cavity volume is treated as the ion volume in the expression for the thermodynamic pressure. However, since the Inferno model is not fully variational there is no available expression allowing one within that model to find the thermodynamic pressure from an explicit derivative of the thermodynamic potential. Although in our approach a cavity is also introduced in order to account for noncentral ions, the cavity radius is a variational variable (see the beginning of Sec IV). Since we do not impose the neutrality of the WS sphere and only require the charge neutrality in the whole space (it assures the locality of the SCF potential) our approach, as mentioned above, needs an "ionization model," i.e., an additional relation between the homogeneous free-electron density n_0 and the first-order variables. Thus in our theory both the neutrality condition and the ionization model have to be respected in the variational procedure. In the TF case we have found that the correct ionization model is $Z-Z^*=\int d^3r[n(\vec{r})-n_0]$, where $n(\vec{r})$ is the first-order electron density. It appears to lead correctly to the classical TF ion-cell model of Ref. [1]. Substituting that ionization model into the neutrality equation, one can see that the cavity radius becomes the WS radius (see Sec. IV). Our variational calculation in the TF case leads to the conclusion that the homogeneous free-electron density n_0 is to be determined from the variational equation stating that the space integral of the electrostatic potential outside the WS sphere is zero. This equation (and its slightly modified versions in the QAA and SC cases) is the main result of our approach. In the TF case this equation appears to be equivalent to the neutrality of the WS sphere (Sec. IV and Appendix B). These TF calculations are relatively straightforward and reflect well the main ideas of our approach. In such a way all basic physical assumptions of our approach can in principle be found in Secs. II–IV.

In the quantum QAA and the SC cases the calculations are more involved but it appears that these cases lead to results that are conceptually identical to the results in the TF case. Again, the only physically acceptable ionization model is the same as in the TF case. [An important point in the paper is the demonstration that other ionization models are unphysical (see Secs. V and VI).] In particular, the conditions allowing one to calculate n_0 in the quantum cases have the same physical meaning as in the TF case (the integral of the electrostatic potential outside the WS sphere equal to zero). However, the important fact is that in our quantum cases the WS sphere is not neutral and the SCF potential is not zero outside the WS sphere. It is decaying there but in general may have oscillations due to the Friedel terms. This is the main difference between the results of our quantum cases QAA and SC and the Inferno model in which the imposed neutrality of the WS sphere leads automatically to the SCF potential, which is identically zero outside the WS sphere.

The relatively involved calculations in our cases QAA (Sec. V) and SC (Sec. VI) are necessary since in these quantum cases the ionization models can contain, at least in principle, not only the first-order electron density but also other first-order structure variables (this is practically impossible in the TF case). With such more complicated ionization models the variational approach should go beyond the usual density functional formalism. However, the reader that is not interested in the details of this demonstration may go directly to the results of Secs. V and VI. The formalism in the SC case (Sec. VI) is based on the same ideas as that of Sec. V with some important differences that are due to averages over superconfigurations.

II. CLUSTER EXPANSION AND THE GENERAL SCHEME

We consider infinite plasma at a temperature T consisting of classical ions (atomic number Z) at ion density equal to

$n_i = N_i/V$, where N_i is the number of ions and V is the volume of the plasma. The electrons are treated quantum mechanically and may be either bound to the ions or free. On average, the medium is neutral and the long-range Coulomb interactions between ions and free electrons are screened. The main idea of the cluster expansion we use [14] is to consider statistically averaged quantities in the form of a series in which each order includes a contribution from the number of interacting ions equal to the order. In such a way the zero-order term corresponds to the contribution from infinite homogeneous electron fluid neutralized by a constant ion background. In the zero-order term no ion center is present. The first-order term corresponds to the contribution of one ion center screened by the plasma, and the second-order term corresponds to all possible contributions of the pairs of two ion centers screened by the plasma, and so on. The cluster expansion automatically assures that in the order p all contributions that are already taken into account in lower orders (i.e., in the order $p-1$, $p-2$, etc.) are correctly subtracted. From the mathematical point of view this subtraction is necessary for the convergence of the cluster expansion.

In this paper we are interested in the construction and minimization of a free-energy functional of the plasma of the element of the atomic number Z, characterized by the temperature T and average ion density n_i. The two first orders (i.e., zero and one) of the cluster expansion of the free energy per unit volume are

$$f(n_i,T,Z) = f_0 + \langle f\rangle_1 + \cdots \quad . \tag{1}$$

The zero-order term is the free-energy density of the homogeneous electron gas (jellium) and depends only on the temperature and on an average free-electron density n_0 that is unknown at this moment and will be determined via the variational procedure. The first-order term is of the form

$$\langle f\rangle_1 = n_i \int d^3r[f_1^{(\text{ion+jellium})}(X;n_i,T,Z|\vec{r}) - f_0(n_0;T)], \tag{2}$$

where $f_1^{(\text{ion+jellium})}(X;n_i,T,Z|\vec{r})$ denotes a functional corresponding to the free-energy density of a nonhomogeneous infinite plasma interacting with and screening one central ion imbedded in the plasma. The ensemble X denotes $X = \{n_0, X_1\}$ where X_1 represents all functions and variables describing the system of the first order, i.e., bound and free electrons interacting with the central ion and with the plasma. We assume that the change of the electron density resulting from the insertion of the central ion is local, i.e., that far from the ion the free-electron density of the system "ion+jellium" will be equal to n_0. In this situation the subtraction of the zero-order free energy per unit volume inside the integral of Eq. (2) may assure the convergence of the first-order term.

In this paper we are interested mainly in the free energy per ion, which is related to the free energy per unit volume as $F = f/n_i$.

This free energy per ion in our approximation will be

$$F(X;n_i,T,Z) = F_0 + \Delta F_1, \tag{3}$$

where

$$F_0 = F_0(n_0;n_i,T) = \frac{f_0(n_0;T)}{n_i} \tag{4}$$

is the free energy of a homogeneous electron gas of an unknown density n_0, occupying the volume of that ion, and

$$\Delta F_1 = \int d^3r[f_1^{(\text{ion+jellium})}(X;n_i,T,Z|\vec{r}) - f_0(n_0;T)]. \tag{5}$$

In the above equation ΔF_1 is the correction to the free energy per ion resulting from the presence of a central ion of the total charge Ze. The central ion is screened by plasma electrons and noncentral ions in such a way that the total charge is zero. The expression for the free energy contains of course the thermodynamic parameters n_i, T, Z. We will construct the free-energy functional in the vicinity of searched equilibrium using an ensemble of functions and variables X describing the electrons and ions. The equilibrium values of X will be found from the minimization of the free energy F with respect to these variables fulfilling some imposed conditions. At equilibrium the value of the free energy per ion will depend only on the values of n_i, T, Z. The approximate expressions for ΔF_1 in three considered cases, having the same form as that in Eq. (5), will be proposed and discussed in the following sections.

As already mentioned, the minimization procedure with respect to n_0 and $\{X_1\}$ will be performed respecting a certain number of conditions, which have the general form

$$C_j(X;n_i,T,Z) = 0, \quad j = 1, \ldots, J. \tag{6}$$

The thermodynamic potential Ω per ion to be minimized is thus of the form

$$\Omega(X;n_i,T,Z) = F(X;n_i,T,Z) - \sum_{j=1,\cdots,J} \lambda_j C_j(X;n_i,T,Z), \tag{7}$$

where λ_j are the Lagrange multipliers.

Since F_0 does not depend on $\{X_1\}$ it is convenient to write Ω in the form

$$\Omega = F_0(n_0;T) + \Delta\Omega_1(n_0,X_1;n_i,T,Z), \tag{8}$$

where

$$\Delta\Omega_1 = \Delta F_1 - \sum_{j=1,\cdots,J} \lambda_j C_j(X;n_i,T,Z). \tag{9}$$

The equilibrium forms and values of the ensemble of functions and variables $X_{eq}(n_i,T,Z)$ is to be found from the equation

$$\frac{\delta\Omega}{\delta X}(X_{eq};n_i,T,Z) = 0. \tag{10}$$

The thermodynamic pressure can be calculated (see Appendix A) from the following known formula:

$$P = - \left. \frac{\partial F(X_{eq}(n_i,T,Z);n_i,T,Z)}{\partial v_i} \right|_{T=\text{const}} = n_i^2 \left. \frac{\partial F(X_{eq}(n_i,T,Z);n_i,T,Z)}{\partial n_i} \right|_{T=\text{const}} = n_i^2 \left(\frac{\partial \Omega(X_{eq};n_i,T,Z)}{\partial n_i} \right)_{\text{explicit}}. \quad (11)$$

The index "explicit" in Eq. (11) means that in the differentiation on the right-hand side (RHS) only the explicit dependence on n_i is taken into account while the dependence on n_i via $X_{eq}(n_i,T,Z)$ has to be disregarded (see Appendix A). Here we use the definition of the volume per ion $v_i = 1/n_i$. Due to the variational character of the equilibrium with respect to all the functions and the variables X, we immediately find

$$P = n_i^2 \left(\frac{\partial \Omega(X_{eq};n_i,T,Z)}{\partial n_i} \right)_{\text{explicit}} = - f_0(n_0;T) + n_i^2 \left(\frac{\partial \Delta\Omega_1(X_{eq};n_i,T,Z)}{\partial n_i} \right)_{\text{explicit}}, \quad (12)$$

which means that the only differentiation that has to be performed in Eq. (12) is upon the explicit dependence of $\Delta\Omega_1$ on the ion density n_i.

Let us note also that in the case of a well-defined equilibrium of a homogeneous gas (at a temperature T, with a known density n_0 and the corresponding chemical potential μ_0), the expression for the thermodynamic pressure is

$$P = - f_0(n_0;T) + n_0\mu_0(n_0;T). \quad (13)$$

Comparing Eqs. (12) and (13), we see that the second term on the RHS of Eq. (12) will in some sense replace the well-known term $n_0\mu_0(n_0;T)$. However, its calculation will involve all the parameters of the equilibrium; that is, n_i,T,Z instead of n_0,T as in the case of the homogeneous electron gas with a given electron density value.

As previously stated, the zero-order term of the potential Ω contains only one variable n_0 and does not depend on the first-order variables X_1. The variational equation with respect to n_0 is the only one that involves both the zero-order term F_0 and the first-order term $\Delta\Omega_1$. It has the form:

$$\frac{1}{n_i}\frac{\delta f_0(n_0)}{\delta n_0} + \frac{\delta \Delta\Omega_1}{\delta n_0} = \frac{\mu_0}{n_i} + \frac{\delta \Delta\Omega_1}{\delta n_0} = 0. \quad (14a)$$

In the previous approaches (that applied in the model Inferno [9,10] and that in the model AJCI [12]) the relation Eq. (14a) is not used: only the first-order contribution $\Delta\Omega_1$ to the thermodynamic potential is considered and the equilibrium equation is

$$\frac{\delta \Delta\Omega_1}{\delta X_1} = 0. \quad (14b)$$

In such a way the number of variational equations in Eq. (14b) is less by one than the number of equations in Eq. (10). What is lacking is an equation allowing one to find the value of n_0. As mentioned above in the Inferno model [9,10], the additional condition for n_0 is the neutrality of the WS sphere. Similarly, the approach AJCI [12] does not allow one to determine the average ionization $Z^* = n_0/n_i$ (equilibrium in this approach is given by four parameters: n_i, T, Z, n_0 and not by the usual three n_i, T, Z).

A. Remark on the virial theorem

Classical and quantum many-particle systems satisfy a virial theorem (see, for instance, Ref. [15]). In a system of particles interacting via the Coulomb potential the virial theorem yields the following relation between the thermodynamic pressure, total volume, and kinetic and potential energies of the system:

$$\frac{3}{2}PV = \langle E_{kin} \rangle + \frac{1}{2}\langle E_{pot} \rangle. \quad (15)$$

The standard proof of the virial theorem applies to exact microscopic many-body systems. In the case of involved approximate self-consistent approaches (as the one presented here in this paper) checking whether the virial theorem is valid is often not straightforward since the potential and kinetic energies cannot be directly identified. In such cases it is convenient to apply the similarity transformation proposed in Ref. [1]. This similarity transformation is based on the following scaling:

$$T \to \lambda T, \quad (16a)$$

$$\vec{r} \to \lambda^{-1/2}\vec{r}, \quad (16b)$$

$$e^2 \to \lambda^{1/2} e^2, \quad (16c)$$

where T, $\vec{r}$, and e^2 are the temperature, the coordinate vector, and the square of the elementary charge, respectively, and λ is the scaling parameter. In our case in which we consider the free energy per ion F, we shall prove that the equilibrium value of F has the following scaling property:

$$F(\lambda^{3/2}n_i, \lambda T, \lambda^{1/2}e^2) = \lambda F(n_i, T, e^2). \quad (17)$$

If this scaling is preserved in the model, the differentiation of Eq. (17) with respect to λ taken at the value $\lambda = 1$, leads to

$$T \left. \left(\frac{\partial F}{\partial T} \right) \right|_{n_i,e^2} + \frac{3}{2} n_i \left. \left(\frac{\partial F}{\partial n_i} \right) \right|_{T,e^2} + \frac{1}{2} e^2 \left. \left(\frac{\partial F}{\partial e^2} \right) \right|_{n_i,T} = F. \quad (18)$$

One can identify the partial derivatives as follows:

$$e^2 \left. \left(\frac{\partial F}{\partial e^2} \right) \right|_{n_i,T} = \langle E_{pot} \rangle / N_i, \quad (19a)$$

$$n_i \left. \left(\frac{\partial F}{\partial n_i} \right) \right|_{T} = - v_i \left. \left(\frac{\partial F}{\partial v_i} \right) \right|_{T} = P v_i, \quad (19b)$$

$$F - T \left. \left(\frac{\partial F}{\partial T} \right) \right|_{n_i} = F + T s_i = u_i, \quad (19c)$$

where P is the thermodynamic pressure, s_i is the entropy per ion, and u_i is the total energy per ion. Substitution of Eqs.

(19) into Eq. (18) leads to the virial theorem,

$$\frac{3}{2}Pv_i = u_i - \frac{1}{2}\langle E_{pot}\rangle / N_i. \tag{20}$$

The scaling property of Eq. (18) has to be directly verified in the self-consistent equations resulting from the variational approach. The physical interpretation of terms from Eq. (18) is simplified when the equilibrium state is fully variational. In our approach in which the equilibrium is variational with respect to all variables X, we have, as in the case of the pressure equation [see Eq. (11) and Appendix A],

$$\left(\frac{\partial F}{\partial T}\right)\Bigg|_{n_i,e^2} = \left(\frac{\partial \Omega(X_{eq};n_i,T,Z,e^2)}{\partial T}\right)_{\text{explicit}}, \tag{21}$$

and

$$\left(\frac{\partial F}{\partial e^2}\right)\Bigg|_{n_i,T} = \left(\frac{\partial \Omega(X_{eq};n_i,T,Z,e^2)}{\partial e^2}\right)_{\text{explicit}}. \tag{22}$$

These identities make the identification of some terms standing on the RHS of Eq. (20) straightforward.

III. ZERO-ORDER OR HOMOGENEOUS ELECTRON GAS

In the zero-order the electron charge density $-en_0$ of the homogeneous electron gas is neutralized by the homogeneous ion charge density of the same absolute value and the opposite sign. In the TF case, when exchange interaction is neglected, the contribution will be the free energy of the noninteracting electron gas at the temperature T and density n_0, $f_0^{(0)}(n_0)$,

$$f_0(n_0) = f_0^{(0)}(n_0). \tag{23}$$

The distribution of the independent-electron gas energy will be in the form of the noninteracting electrons, i.e., of the Fermi-Dirac form,

$$n_0 = \frac{2}{(2\pi)^3}\int d^3k \frac{1}{e^{\beta(\varepsilon_k-\mu_0)}+1}, \tag{24}$$

where $\beta = 1/T$, the factor 2 accounts for the spin degeneracy

$$\varepsilon_k = \frac{(\hbar k)^2}{2m}, \tag{25}$$

and μ_0 is the free-electron chemical potential, unknown at the moment [directly related to the density n_0 by Eq. (24)]. The zero-order free energy of the independent electron gas per unit volume $f_0^{(0)}(n_0)$ is therefore

$$f_0^{(0)}(n_0) = \frac{2}{(2\pi)^3}\int d^3k (n_k^{(0)}\varepsilon_k - TS_k^{(0)}), \tag{26}$$

where

$$S_k^{(0)} = -[n_k^{(0)}\ln(n_k^{(0)}) + (1-n_k^{(0)})\ln(1-n_k^{(0)})], \tag{27}$$

and

$$n_k^{(0)} = \frac{1}{\exp[\beta(\varepsilon_k - \mu_0)]+1}. \tag{28}$$

In the quantum average atom and in the superconfigurations cases considered in the following sections the zero-order term will not only contain the $f_0^{(0)}(n_0)$ term but will also take into account a density-functional-theory (DFT) exchange-correlation free energy $f_{xc}(n_0)$. So in these two cases we will have

$$f_0(n_0) = f_0^{(0)}(n_0) + f_{xc}(n_0). \tag{29}$$

In practice we will use for $f_{xc}(n_0)$ the local-density exchange-correlation approximation as given in Ref. [16].

IV. THOMAS-FERMI MODEL OF THE FIRST-ORDER FREE ENERGY

We will follow here Mermin's approach [17] to the TF finite temperature theory as a particular case of the DFT. In the first order the density of electron gas is modified by the central charge and will be characterized by the distribution function

$$n_k^{(1)}(\vec{r}) = \frac{1}{\exp[\beta(\varepsilon_k - e^2V(\vec{r}) - \mu_0)]+1}, \tag{30}$$

where $V(\vec{r})$ is a trial variable that is local and tends to zero for large $r=|\vec{r}|$ sufficiently fast. In such a way $n_k^{(1)}(\vec{r}) \underset{r\to\infty}{\longrightarrow} n_k^{(0)}$. The first-order electron density $n(\vec{r})$ is equal to

$$n(\vec{r}) = \frac{2}{(2\pi)^3}\int d^3k n_k^{(1)}(\vec{r}). \tag{31}$$

Far from the center the ion homogeneous distribution (coming from the ions other than the central ion) neutralizes the electron charge distribution. We assume that this occurs starting from a radius R (unknown at this moment) from the ion center. We introduce therefore a cavity around the central ion to which the charge distribution from ions other than the central ion does not enter. The correction with respect to the charge density of the zero order is as follows: change of the electron charge density,

$$-e[n(\vec{r}) - n_0],$$

change of the noncentral ions charge density,

$$e[n_0\theta(r-R) - n_0],$$

total change of the charge density,

$$\rho_{\text{total}}^{(1)}(\vec{r}) = Ze\delta(\vec{r}) - e[n(\vec{r}) - \theta(r-R)n_0]. \tag{32}$$

According to the general scheme and Eq. (2) the change of the free energy due to the presence of the additional charges will be given by the following formula:

$$\Delta F_{1,TF}=\Delta F^{(0)}_{1,TF}+\Delta F_{1,el}, \tag{33}$$

where $\Delta F^{(0)}_{1,TF}$ accounts for the correction of the kinetic energy and of the entropy terms and $\Delta F_{1,el}$ is the electrostatic interaction term,

$$\Delta F^{(0)}_{1,TF}[n_0,V(\vec{r}),R;T,n_i,Z]=\int d^3r\frac{2}{(2\pi)^3}\int d^3k\{\varepsilon_k[n_k^{(1)}(\vec{r})-n_k^{(0)}]-T[S_k^{(1)}(\vec{r})-S_k^{(0)}]\}, \tag{34}$$

where

$$S_k^{(1)}(\vec{r})=-[n_k^{(1)}(\vec{r})\ln[n_k^{(1)}(\vec{r})]+[1-n_k^{(1)}(\vec{r})]\ln[1-n_k^{(1)}(\vec{r})]], \tag{35}$$

and

$$\Delta F_{1,el}=\int d^3r\left[[n(\vec{r})-\theta(r-R)n_0]\left(-\frac{Ze^2}{r}+\frac{e^2}{2}\int d^3r'\frac{[n(\vec{r}\,')-\theta(r'-R)n_0]}{|\vec{r}-\vec{r}\,'|}\right)\right]. \tag{36}$$

It is supposed that the expressions in Eqs. (34)–(36) are well defined, i.e., they are finite. This is assured by the local neutrality. In order that our model be correct the total charge introduced in the first order should be zero, i.e., we shall have

$$\int d^3r\,\rho^{(1)}_{\text{total}}(\vec{r})=0 \quad \text{or} \quad Z-\int d^3r[n(\vec{r})-n_0]-\frac{4\pi R^3 n_0}{3}=0. \tag{37}$$

A. TF ionization model

The important point is now to relate the value of n_0, which is the average free-electron density with the first-order density $n(\vec{r})$ and with the ion density. The free-electron density is the density of these electrons that can be found far from the central ion. We choose the following condition:

$$\frac{n_0}{n_i}=Z-\int d^3r[n(\vec{r})-n_0]. \tag{38}$$

The left-hand side is the number of the free electrons per ion. The right-hand side is the difference between the total number of electrons per ion, Z, and the number of electrons that are "bound" to the ion. In the TF model this definition seems to be natural since in that model there is no distinction between bound and free electrons. It also corresponds well to the scheme of the cluster expansion.

B. Functional to be minimized in the TF case

In principle the two constraints, the neutrality condition Eq. (37) and the ionization model, i.e., Eq. (38), should be used in the construction of the thermodynamic potential Ω_{TF}. However, with our choice of the ionization model substituting Eq. (38) into Eq. (37) gives immediately

$$\frac{n_0}{n_i}=\frac{4\pi R^3 n_0}{3} \quad \text{or} \quad n_i=\frac{3}{4\pi R^3}, \tag{39}$$

which means that R is the Wigner-Seitz radius. In such a way we will only include into the potential Ω_{TF} the equation corresponding to the ionization model, i.e., Eq. (38), with a corresponding Lagrange multiplier that we call γ. Thus the thermodynamics potential becomes

$$\Omega_{TF}(n_0,V(\vec{r});n_i,T,Z)=\frac{f_0(n_0;T)}{n_i}+\Delta F_{1,TF}(n_0,V(\vec{r});n_i,T,Z)-\gamma\left(\frac{n_0}{n_i}-\left[Z-\int d^3r[n(\vec{r})-n_0]\right]\right), \tag{40}$$

where the radius R is given by formula (39).

C. TF variational principle

At equilibrium Ω_{TF} has to be stationary with respect to n_0 and $V(\vec{r})$. We calculate the derivates using the fact that at fixed n_0 the potential Ω_{TF} is a functional of $n(\vec{r})$ [see Eq. (40) and Ref. [17]]. We may thus write $\Omega_{TF}(n_0,V(\vec{r});n_i,T,Z)$ $=\Omega'_{TF}(n_0,n(\vec{r});n_i,T,Z)$ and calculate

$$\left.\frac{\delta\Omega_{TF}}{\delta V(\vec{r})}\right|_{n_0=\text{const}}=\int d^3r'\left(\left.\frac{\delta\Omega'_{TF}}{\delta n(\vec{r}\,')}\right|_{n_0=\text{const}}\left.\frac{\delta n(\vec{r}\,')}{\delta V(\vec{r})}\right|_{n_0=\text{const}}\right)=0, \tag{41}$$

$$\left.\frac{\delta\Omega_{TF}}{\delta n_0}\right|_{V(\vec{r})=\text{const}}=\int d^3r\left(\left.\frac{\delta\Omega'_{TF}}{\delta n(\vec{r})}\right|_{n_0=\text{const}}\left.\frac{\delta n(\vec{r})}{\delta n_0}\right|_{V(\vec{r})=\text{const}}\right)+\left.\frac{\delta\Omega'_{TF}}{\delta n_0}\right|_{n(\vec{r})=\text{const}}=0. \tag{42}$$

From Eq. (41), Eq. (30), and Eq. (31), we get immediately

$$\left.\frac{\delta\Omega'_{TF}}{\delta n(\vec{r})}\right|_{n_0=\text{const}}\left.\frac{\delta n(\vec{r})}{\delta V(\vec{r})}\right|_{n_0=\text{const}}=0, \tag{43}$$

due to the fact that

$$\left.\frac{\delta n(\vec{r}\,')}{\delta V(\vec{r})}\right|_{n_0=\text{const}}=\delta(\vec{r}-\vec{r}\,')\left.\frac{\delta n(\vec{r})}{\delta V(\vec{r})}\right|_{n_0=\text{const}}$$

[see Eqs. (30) and (31)] and since $\delta n(\vec{r})/\delta V(\vec{r})|_{n_0=\text{const}}$ is nonzero [see again Eqs. (30) and (31)] we should have

$$\left.\frac{\delta\Omega'_{TF}}{\delta n(\vec{r})}\right|_{n_0=\text{const}}=0. \tag{44}$$

The last derivatives can be easily calculated (see also Ref. [17]).

$$\frac{\delta\Omega'_{TF}}{\delta n(\vec{r})}=e^2V(\vec{r})+\mu_0-e^2V_{el}(\vec{r})-\gamma, \tag{45}$$

where we defined the potential due to the electrostatic interaction as

$$e^2V_{el}(\vec{r}) = \left(\frac{Ze^2}{r} - e^2\int d^3r' \frac{[n(\vec{r}\,') - \theta(r'-R)n_0]}{|\vec{r}-\vec{r}\,'|}\right). \tag{46}$$

We get from Eqs. (45) and (44),

$$e^2V(\vec{r}) - e^2V_{el}(\vec{r}) = -\mu_0 + \gamma. \tag{47a}$$

From the fact that both $V(\vec{r})$ and $V_{el}(\vec{r})$ tend to zero for $r \to \infty$ [from the assumption of the locality and the neutrality Eq. (37), respectively] we arrive finally at the equations

$$V(\vec{r}) = V_{el}(\vec{r}), \tag{47b}$$

$$\gamma = \mu_0. \tag{47c}$$

We also see that due to Eq. (44) the first term on the RHS of Eq. (42) is identically zero. One can calculate directly (see also Ref. [17]),

$$\frac{\delta f_0^{(0)}(n_0;T)}{\delta n_0} = \mu_0$$

and get from Eq. (42) with Eq. (47),

$$\frac{\mu_0-\gamma}{n_i} + \int d^3r[\gamma - \mu_0 + \theta(r-R)e^2V_{el}(\vec{r})] = \int d^3r\ \theta(r-R)e^2V(\vec{r}) = 0. \tag{48}$$

It is easy to check that the well-known solution of the TF ion-in-cell model considered in Ref. [1] fulfills the just obtained equations of our model with the TF form of the first order ΔF_1 and with the ionization model of Eq. (38). In the TF model of Ref. [1] the WS sphere is neutral, the potential is zero at the WS radius, and is identically zero outside the sphere. This potential is calculated from the same Poisson equation as our Eq. (46) but is limited to the region inside the WS sphere and with the boundary condition $dV(r)/dr|_{r=R_{WS}}=0$. Moreover, it appears also that the TF ion-in-cell model of Ref. [1] is the unique solution fulfilling our system of self-consistent equations, Eqs. (30), (31), (46), (47b), and (48). This equivalence is discussed in Appendix B [18]. In this way in the TF case we get the neutrality of the WS sphere, the potential that is identically zero outside the sphere and the first-order electron density that is equal to the average (asymptotic) electron density outside the sphere. The chemical potential μ_0 and consequently the average electron n_0 density are determined from the neutrality of the WS sphere,

$$\int_{r\le R_{WS}} d^3r n(\vec{r}) = \int_{r\le R_{WS}} d^3r \frac{2}{(2\pi)^3}\int d^3k \frac{1}{e^{\beta[\varepsilon_k - e^2V(\vec{r})-\mu_0]}+1} = Z. \tag{49}$$

D. Pressure calculation in the TF case

According to the general scheme [see Eq. (11) and Appendix A] we calculate pressure from the standard thermodynamic definition,

$$P_{TF} = n_i^2 \frac{\partial F_{TF}}{\partial n_i}\bigg|_{T=\text{const}} = n_i^2\frac{\partial \Omega_{TF}}{\partial n_i}\bigg|_{\text{explicit}}, \tag{50}$$

where we use the variational property of the equilibrium state. Let us note that in the TF case,

$$\frac{\delta\Omega_{TF}(n_0,[V(r)];R(n_i),T,Z,n_i)}{\delta R(n_i)} = \frac{\delta}{\delta R(n_i)}\int d^3r\ \theta[r-R(n_i)]e^2V(\vec{r}) = -4\pi n_0 R(n_i)^2 V[R(n_i)] = 0. \tag{51}$$

Immediately we get from Eqs. (51), (42), and (47),

$$P = [-f_0(n_0) + n_0\mu_0(n_0)]|_{n_0=n_{0,eq}}, \tag{52}$$

where $n_{0,eq}=n_{0,eq}(T,n_i,Z)$ is the equilibrium solution and μ_0 can be obtained from n_0 using Eq. (24). In Eq. (52) we find the same expression as that in Ref. [1] (see also Ref. [19]). We recover in this way the expression for pressure formally identical to the expression for the pressure of an ideal gas except that the average electron density and chemical potential of that gas are now calculated from the SCF TF model. The EOS data based on the ion-in-cell TF model are being widely used among the dense plasma community (see, for instance, Ref. [20]).

Other definitions different from Eq. (38) for the number of "bound" electrons in our TF case do not lead to the standard Thomas-Fermi ion-in-cell model at finite temperature. In fact Eq. (38) does not make use of any division of electrons into bound and free; such a division does not appear in a natural way in the Thomas-Fermi model. Sometimes, however, in the literature are used expressions for the bound electrons in which the bound electrons are defined as those that have the total energy negative,

$$\frac{(\hbar k)^2}{2m} - e^2V(\vec{r}) < 0. \tag{53}$$

One may try to put the number of bound electrons Z_b into the expression for n_0 using for Z_b the following definition:

$$Z_b = \frac{2}{(2\pi)^3}\iint_{\varepsilon_k - \Delta\mu(\vec{r})\le 0} d^3r\, d^3k \frac{1}{e^{\beta[\varepsilon_k - \Delta\mu(\vec{r})-\mu_0]}+1}. \tag{54a}$$

Consequently, Eq. (38) would be replaced by its new version,

$$\frac{n_0}{n_i} = Z - Z_b. \tag{54b}$$

One can easily check that the choice of Eqs. (54a) and (54b) in our variational formulation does not give the Thomas-Fermi model.

V. QUANTUM AVERAGE ATOM IN PLASMA

The result of Sec. IV can be considered as a good test of our variational principle. The TF case (i.e., our variational approach with the TF expressions for the first-order ion free energy) leads to the classical result of the TF finite temperature ion-in-cell model [1,19]. An important role in the derivation plays the ionization model that in the TF case has been chosen in the form of Eq. (38). This result gives us confidence as concerns possible extensions of our approach to the quantum atoms and superconfigurations in plasmas.

In this section we will now consider the QAA case. We assume that the first-order free energy can be approximated by the expression corresponding to a quantum nonhomogeneous noninteracting electron gas in a local, bounded (i.e., having a finite support) potential $V(\vec{r})$. This potential is unknown at the moment. In this approximation the electron density $n(\vec{r})$ is

$$n(\vec{r}) = 2\sum_{s\in B} n_s|\psi_s(\vec{r})|^2 + \frac{2}{(2\pi)^3}\int d^3k\, n_k|\psi_{\vec{k}}(\vec{r})|^2. \tag{55}$$

The bound states of $V(\vec{r})$ have indices $s \in B$ (their number will be finite due to the potential locality). Their eigenvalues, occupations, and the wave functions will be, respectively, ε_s, n_s, and $\psi_s(\vec{r})$. The presence of the potential will also modify the wave function of the free states.

A question appears: What ionization model should be used in the QAA case? The first possibility is to use in our QAA case the same ionization model as in the TF case, i.e., Eq. (38). Then, since this ionization model is expressed as a functional of electron density one may use principles of the DFT approach. Although the calculation is more involved in the quantum DFT case it follows the main lines of that in the TF case.

However, in the quantum case there are two categories of electrons and, in principle, other ionization models [i.e., other than that of Eq. (38)] could also be considered. In particular, in the quantum cases there is a natural division of one-electron states into bound and free. In this situation another natural ionization model could be the following one:

$$\frac{n_0}{n_i} = Z - Z_b, \tag{56a}$$

with the bound electron number Z_b defined as

$$Z_b = 2\sum_{s\in B} n_s\int d^3r|\psi_s(\vec{r})|^2 = 2\sum_{s\in B} n_s, \tag{56b}$$

and where the sum is over all the bound spectrum B of the SCF potential. The factor 2 corresponds to the spin degeneracy. The ionization model of Eqs. (56a) and (56b) seems to be intuitively justified since only the bound electron states are local. All free electron states have asymptotic behavior of outgoing waves and are not localized.

In general, any ionization model can be expressed in the form of Eq. (56a) with a more general definition of Z_b. Assuming that this quantity can be expressed entirely in terms of the first-order variables and of the average electron density n_0, one can write it in the following form:

$$Z_b = Z_b'[n_0, V(\vec{r}), \{n_s\}, \{n_k\}] = Z_b[n_0, n(\vec{r}), \{n_s\}, \{n_k\}]. \tag{56c}$$

In the following consideration we will use the last term on the RHS of Eq. (56c) since due to its dependence on the electron density $n(\vec{r})$ it contains as special cases two ionization models that seem to be physically sound: the one used in the TF case [Eq. (38)] and the above-mentioned ionization model Eq. (56b). We will show, however, below that, ionization models other than the ionization model of Eq. (38) lead to solutions in which the chemical potentials for bound and free electrons are different, i.e., to solutions that are not acceptable from the point of view of the physical coherence. General ionization models such as, Eqs. (56b) and (56c) may distinguish and treat differently bound and free electrons. In such a way they contain, in general, expressions that are not simple functionals of the first-order density $n(\vec{r})$ at fixed n_0. Thus in order to see what consequences may have such models, one shall use a variational approach that goes beyond the DFT approach. For that reason we will use in what follows a more general variational approach in which the variables will be the potential $V(\vec{r})$ and the bound and free occupation numbers. In such a way the bound and free-state occupations numbers n_s and n_k are at the moment arbitrary. In that situation the electron density given in Eq. (55) does not, in general, correspond to an electron density of a noninteracting electron gas at equilibrium. We require, however, that far from the ion center the density $n(\vec{r}) \xrightarrow[r\to\infty]{} n_0$, i.e., far from the central ion the electron charge distribution becomes $-en_0$ that is the same as that of the zero order (with the constant n_0 that has to be determined). The bound and free wave functions fulfill the Schrödinger equation with the potential $-e^2V(\vec{r})$,

$$\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 - e^2V(\vec{r})\right)\begin{pmatrix}\psi_s(\vec{r})\\ \psi_{\vec{k}}(\vec{r})\end{pmatrix} = \begin{pmatrix}\varepsilon_s\psi_s(\vec{r})\\ \varepsilon_{|\vec{k}|}\psi_{\vec{k}}(\vec{r})\end{pmatrix}. \tag{57}$$

The free-electron wave functions are normalized as are the plane waves to the delta functions in the $\vec{k}$ space,

$$\int d^3r\, \psi^*_{\vec{k}}(\vec{r})\psi_{\vec{k}'}(\vec{r}) = (2\pi)^3\delta(\vec{k}-\vec{k}'). \tag{58a}$$

This leads (see, for instance, Ref. [9]) to the equation that can be also considered as the normalization condition of the free electron states,

$$\int d^3r(|\psi_{\vec{k}}(\vec{r})|^2 - 1) = C_{\vec{k}}, \tag{58b}$$

with $C_{\vec{k}}$ being finite for each $\vec{k}$. The bound wave functions are normalized to unity.

A. First-order free energy per ion in the QAA case

In the chosen approximation the correction to the free energy resulting from the presence of the central ion, of the ion cavity and of the response of the electron gas to this presence, is of the form

$$\Delta F_{1,QAA}(n_0,V(\vec{r}),R;T,Z) = \Delta F^{(0)}_{1,QAA} + \Delta F_{1,el} + \Delta F_{1,xc}, \tag{59}$$

where

$$\Delta F^{(0)}_{1,QAA} = 2\sum_{s\in B}\left[n_s \int d^3r\, \psi^*_s(\vec{r})\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi_s(\vec{r})\right) - TS_s\right] + \int d^3r\left(\frac{2}{(2\pi)^3}\int d^3k\left\{n^{(0)}_k\left[\psi^*_{\vec{k}}(\vec{r})\left(-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi_{\vec{k}}(\vec{r})\right) - \varepsilon_k\right] - TS^{(0)}_k|\psi_{\vec{k}}(\vec{r})|^2\right\} - f^{(0)}_0(n_0)\right). \tag{60a}$$

$\Delta F_{1,el}$ has the same form as in Eq. (36), and

$$\Delta F_{1,xc} = \int d^3r\{f_{xc}[n(\vec{r}) - f_{xc}(n_0)]\} \tag{60b}$$

is the exchange-correlation term.

In Eq. (60a),

$$S_a = -[n_a\ln(n_a) + (1-n_a)\ln(1-n_a)] \tag{60c}$$

is the entropy of electron states with $a\in B$ or $a\in F$.

For the locality of the potential it is necessary that the total charge be zero, which means also that the integrals in Eqs. (36) and (60a) exist. As already mentioned, the exchange-correlation correction will always be considered in the local-density-approximation (LDA) approach, i.e., as a function of the local density [16].

As indicated in the general scheme, the free energy per one ion (being the sum of the zero- and the first-order free energies) can be thus written as

$$F_{QAA}(n_0,V(\vec{r}),\{n_s\},\{n_k\},R;T,n_i,Z) = \frac{f_0(n_0;T)}{n_i} + \Delta F_{1,QAA}(n_0,V(\vec{r}),\{n_s\},\{n_k\},R;T,Z). \tag{61}$$

The factors $1/n_i$ multiplying the homogeneous electron gas free-energy term corresponds to the volume occupied by each ion.

B. Functional to be minimized in the QAA case and variational equations in the first order

We start our considerations on the variational method assuming the general ionization model of Eq. (56c). Thus in the QAA case the general form of the functional corresponding to the thermodynamic potential is

$$\Omega_{QAA}(n_0,V(\vec{r}),\{n_s\},\{n_k\},R;n_i,T,Z) = \frac{f_0(n_0;T)}{n_i} + \Delta F_{1,QAA}(n_0,V(\vec{r}),\{n_s\},\{n_k\},R;T,Z) - \gamma\left(\frac{n_0}{n_i} - Z + Z_b(n_0,n(\vec{r}),\{n_s\},\{n_k\})\right) - \lambda\left(Z - \int d^3r[n(\vec{r}) - n_0] - \frac{4\pi R^3 n_0}{3}\right), \tag{62}$$

where γ and λ are Lagrange multipliers.

The equilibrium has to be constructed by variational calculation with respect to all variables: $V(\vec{r})$, all n_s, all n_k, R, and n_0. As previously stated, the variation with respect to the last variable is the only one that involves both the zero- and the first-order contribution to the thermodynamic potential of Eq. (62). We will first consider the variation calculation of the first order $\Delta\Omega_{1,QAA}$. The SCF equations at equilibrium describing the ion structure at fixed n_0 will be found from the stationarity of the potential $\Delta\Omega_{1,QAA}$ with respect to the first-order variables, namely,

$$\frac{\delta\Delta\Omega_{1,QAA}}{\delta V(\vec{r})} = 0, \quad \frac{\delta\Delta\Omega_{1,QAA}}{\delta n_s} = 0, \frac{\delta\Delta\Omega_{1,QAA}}{\delta n_k} = 0, \quad \frac{\delta\Delta\Omega_{1,QAA}}{\delta R} = 0, \tag{63}$$

where the derivatives with respect to the occupation numbers cover all states bound $s\in B$ and free $\vec{k}\in F$. It is assumed that the occupation numbers of the free states depend only on the wave number k. For the calculation of the functional derivative $\delta\Delta F^{(0)}_{1,QAA}/\delta V(\vec{r})$ at constant occupations numbers and at constant average density n_0, we use the following identity:

$$\frac{\delta\Delta F^{(0)}_{1,QAA}}{\delta V(\vec{r})} = \sum_{s\in B}\int d\vec{r}'\left(\frac{\delta\Delta F^{(0)}_{1,QAA}}{\delta\psi_s(\vec{r}')}\frac{\delta\psi_s(\vec{r}')}{\delta V(\vec{r})} + \frac{\delta\Delta F^{(0)}_{1,QAA}}{\delta\psi^*_s(\vec{r}')}\frac{\delta\psi^*_s(\vec{r}')}{\delta V(\vec{r})}\right) + \frac{1}{(2\pi)^3}\int d\vec{k}\int d\vec{r}'\left(\frac{\delta\Delta F^{(0)}_{1,QAA}}{\delta\psi_{\vec{k}}(\vec{r}')}\frac{\delta\psi_{\vec{k}}(\vec{r}')}{\delta V(\vec{r})} + \frac{\delta\Delta F^{(0)}_{1,QAA}}{\delta\psi^*_{\vec{k}}(\vec{r}')}\frac{\delta\psi^*_{\vec{k}}(\vec{r}')}{\delta V(\vec{r})}\right). \tag{64}$$

The expressions for functional derivatives of the wave functions with respect to the potential and the details of the calculations are given in Appendix C. The result can be presented in the following form:

$$\frac{\delta\Delta F^{(0)}_{1,QAA}}{\delta V(\vec{r})} = -2e^4 \underset{a\in B,F}{(S)}\;\underset{b\in B,F}{(S)}\left(\frac{n_a-n_b}{\varepsilon_a-\varepsilon_b}\right)V_{ab}\psi_a(\vec{r})\psi^*_b(\vec{r}) - 2e^2\int\frac{d^3k}{(2\pi)^3}|\psi_k(\vec{r})|^2\frac{\delta n_k}{\delta\varepsilon_k}\left[\varepsilon_k + \ln\left(\frac{n_k}{1-n_k}\right)\right], \tag{65}$$

with $a\neq b$ when both $a,b\in B$ and where the operator $\underset{a\in B,F}{(S)}$ is to be understood as

$$\underset{a\in B,F}{\left(S\right)} = \begin{cases} \displaystyle\sum_{s\in B} & \text{if } a = s \in B, \\ \displaystyle\frac{1}{(2\pi)^3}\int d^3k & \text{if } a = \vec{k} \in F, \end{cases} \tag{66}$$

and

$$V_{ab} = \int d^3r\, \psi_a^*(\vec r)V(\vec r)\psi_b(\vec r). \tag{67}$$

Taking into account the remaining terms in $\Delta\Omega_{1,QAA}$ we get (see Appendix C)

$$\frac{\delta\Delta\Omega_{1,QAA}}{\delta V(\vec r)} = -2e^4 \underset{a\in B,F}{\left(S\right)}\ \underset{b\in B,F}{\left(S\right)} \left(\frac{n_a-n_b}{\varepsilon_a-\varepsilon_b}\right)\Delta V_{ab}\psi_a(\vec r)\psi_b^*(\vec r) - 2e^2\int\frac{d^3k}{(2\pi)^3}|\psi_k(\vec r)|^2\frac{\delta n_k}{\delta\varepsilon_k}\tilde\mu_k = 0, \tag{68}$$

and we denote

$$\Delta V_{ab} = \int d^3r\, \psi_a^*(\vec r)\Delta V(\vec r)\psi_b(\vec r). \tag{69a}$$

The potential difference function standing in Eqs. (69) is equal to

$$\Delta V(\vec r) = V(\vec r) - V_{in}(\vec r) - \gamma\{H_{Z_b}[n(\vec r)] - H_{Z_b}(n_0)\}, \tag{69b}$$

where $V_{in}(\vec r)$, the interaction potential, contains the usual electrostatic and exchange-correlation terms

$$e^2V_{in}(\vec r) = e^2V_{el}(\vec r) - \{v_{xc}[n(r)] - v_{xc}(n_0)\}, \tag{70}$$

where $V_{el}(\vec r)$ is defined as in the TF case [see Eq. (46)] while the contribution that is multiplied by γ is defined as [see Eq. (56c) and Appendix C]

$$H_{Z_b}[n(\vec r)] \equiv \left.\frac{\delta Z_b(n_0,n(\vec r),\{n_s\},\{n_k\})}{\delta n(\vec r)}\right|_{n_0,\{n_s\},\{n_k\}=\text{const}}. \tag{71}$$

The parameter $\tilde\mu_k$ is defined as (a can be bound or free)

$$\tilde\mu_a = \varepsilon_a + v_{xc}(n_0) - \gamma H_{Z_b}(n_0) + \lambda + T\ln\left(\frac{n_a}{1-n_a}\right). \tag{72}$$

From the variations with respect to the bound and free occupation numbers we get

$$\frac{\delta\Delta\Omega_{1,QAA}}{\delta n_s} = 2\tilde\mu_s + 2e^2\int d^3r|\psi_s(\vec r)|^2\Delta V(\vec r) - \gamma\left.\frac{\delta Z_b(n_0,n(\vec r),\{n_s\},\{n_k\})}{\delta n_s}\right|_{n_0,n(\vec r),\{n_k\}=\text{const}} = 0, \tag{73}$$

$$\frac{\delta\Delta\Omega_{1,QAA}}{\delta n_k} = \frac{2}{(2\pi)^3}\int d^3r|\psi_{\vec k}(\vec r)|^2(e^2\Delta V(\vec r) + \tilde\mu_k) - \gamma\left.\frac{\delta Z_b(n_0,n(\vec r),\{n_s\},\{n_k\})}{\delta n_k}\right|_{n_0,n(\vec r),\{n_s\}=\text{const}} = 0. \tag{74}$$

Finally, from the last of Eqs. (63) we obtain

$$\frac{\delta\Delta\Omega_{1,QAA}}{\delta R} = -4\pi R^2n_0e^2V_{el}(R) + 4\pi R^2n_0\lambda = 0. \tag{75}$$

The last equation gives immediately the expression for the Lagrange multiplier λ,

$$\lambda = e^2V_{el}(R). \tag{76}$$

C. Restrictions on ionization models stemming from variational first-order QAA equation

We will now analyze the obtained equations for the SCF calculation [Eqs. (66), (73), (74), and (76)] of the first-order variables at fixed n_0. We will show that the requirements of physical coherence in the QAA model with cavity allows one to use only one ionization model: the ionization model given in Eq. (38), i.e., the same that appeared to be successful in the Thomas-Fermi case considered in the Sec. IV.

Let us define the operator defined by the following matrix:

$$A_{ab} = -2e^2\begin{cases} \left(\dfrac{n_k-n_{k'}}{\varepsilon_k-\varepsilon_{k'}}\right)\Delta V_{\vec k\vec k'}\psi_{\vec k}(\vec r)\psi_{\vec k'}^*(\vec r) + \dfrac{\delta n_k}{\delta\varepsilon_k}\dfrac{\tilde\mu_k}{e^2}|\psi_{\vec k}(\vec r)|^2\delta(\vec k-\vec k'), & a = \vec k\in F,\ b = \vec k'\in F \\ \left(\dfrac{n_a-n_b}{\varepsilon_a-\varepsilon_b}\right)\Delta V_{ab}\psi_a(\vec r)\psi_b^*(\vec r) & \text{when at least one of } a,b\notin F. \end{cases} \tag{77}$$

The matrix A is Hermitian since $A^{+}=A$ and can be diagonalized by an operator U such that $U^{+}U=UU^{+}=I$. The result of the diagonalization is $UAU^{+}=B$, where B is diagonal. Eq. (68) can now be written in the form

$$\begin{aligned}\frac{\delta\Delta\Omega_{1,QAA}}{\delta V(\vec{r})} &= \underset{a\in B,F}{(S)}\ \underset{b\in B,F}{(S)} A_{ab}\psi_a(\vec{r})\psi_b^{*}(\vec{r}) \\ &= \underset{a\in B,F}{(S)}\ \underset{b\in B,F}{(S)} \psi_b^{*}(\vec{r})(U^{+}BU)_{ab}\psi_a(\vec{r}) \\ &= \underset{c\in B,F}{(S)} B_{cc}|[U^{+}\psi(\vec{r})]_c|^2 = 0, \end{aligned} \tag{78}$$

where $\psi(\vec{r})$ is a shorthand notation for the vector

$$\psi_c(\vec{r}) = \begin{cases} \psi_s(\vec{r}), & c = s \in B \\ \psi_{\vec{k}}(\vec{r}), & c = \vec{k} \in F. \end{cases} \tag{79}$$

In order that the spatial-dependent operator in the last term of Eq. (78) be zero one should have $B_{cc}=0$. This means that the whole operator A has to be equal to zero. Let us now note that the operator A as defined by the Eq. (77) is composed of well-separated diagonal and off-diagonal parts. Both parts should be equal to zero and that is possible only if

$$\Delta V_{ab} = 0 \quad \text{for } a \neq b, \tag{80a}$$

and

$$\tilde{\mu}_k = 0 \quad \text{for all } k. \tag{80b}$$

Let us recall that the bound and free wave functions fulfill the completeness relation

$$\sum_{s\in B}\psi_s^{*}(\vec{r})\psi_s(\vec{r}\,') + \int \frac{d^3k'}{(2\pi)^3}\psi_{\vec{k}'}^{*}(\vec{r})\psi_{\vec{k}'}(\vec{r}\,') = \delta(\vec{r}-\vec{r}\,'). \tag{81}$$

Let us multiply Eq. (81) by $\psi_{\vec{k}}^{*}(\vec{r}\,')\Delta V(\vec{r}\,')$ and integrate with respect to $\vec{r}\,'$,

$$\sum_{s\in B}\psi_s^{*}(\vec{r})\langle\psi_{\vec{k}}|\Delta V|\psi_s\rangle + \int \frac{d^3k'}{(2\pi)^3}\psi_{\vec{k}'}^{*}(\vec{r})\langle\psi_{\vec{k}}|\Delta V|\psi_{\vec{k}'}\rangle = \psi_{\vec{k}}^{*}(\vec{r})\Delta V(\vec{r}). \tag{82}$$

In such a way if all $\Delta V_{\vec{k}s}=0$ and for a given $\vec{k}$ all $\Delta V_{\vec{k}\vec{k}'}=0$ then

$$\Delta V(\vec{r}) = 0, \tag{83}$$

except perhaps in the zeros of $\psi_{\vec{k}}^{*}(\vec{r})$. However, the ensemble of zeros of $\psi_{\vec{k}}^{*}(\vec{r})$ has the measure equal to zero in the coordinate space. Except the element $\vec{r}=0$, the ensembles of zeros of $\psi_{\vec{k}}^{*}(\vec{r})$ and $\psi_{\vec{k}_1}^{*}(\vec{r})$ have no common part if $\vec{k}\neq\vec{k}_1$ so Eq. (83) gives for the localized potential $V(\vec{r})$ the following solution

$$V(\vec{r}) = V_{in}(\vec{r}) + \gamma\{H_{Z_b}[n(\vec{r})] - H_{Z_b}(n_0)\}. \tag{84}$$

The interaction potential $V_{in}(\vec{r})$ has a well-established physical sense and has been already found in previous approaches (see Refs. [9–12]). The second part with γ does not correspond to any realistic physical interactions. This term disappears identically in two situations. We discuss these cases and their consequences below.

Case (a). The first situation is when $Z_b(n_0,n(\vec{r}),\{n\},\{n_k\})$ is a linear functional of the first-order density $n(\vec{r})$. This is the case of the ionization model of Eq. (38) for which we have

$$Z_b[n_0,n(\vec{r}),\{n_s\},\{n_k\}] = \int d^3r[n(\vec{r}) - n_0] \tag{85a}$$

that immediately leads to $H_{Z_b}[n(\vec{r})]=1$ and to

$$H_{Z_b}(n[\vec{r}]) - H_{Z_b}(n_0) = 0 \tag{85b}$$

[see Eq. (71)].

We note that Eq. (80b), the second equation stemming from the stationarity of $\Delta\Omega_1$ with respect to the potential, gives in the present case

$$\tilde{\mu}_k = \varepsilon_k + v_{xc}(n_0) - \gamma + \lambda + T\ln\left(\frac{n_k}{1-n_k}\right) = 0 \tag{86a}$$

since we have $H_{Z_b}(n_0)=1$.

Equation (86a) leads to the Fermi-Dirac occupation of the free states, i.e., to

$$n_k = n_k^{(0)}, \tag{86b}$$

since asymptotically the first-order density $n(\vec{r})$ tends to n_0 for large r. That gives the following equation involving the Lagrange multipliers

$$\gamma - \lambda = \mu_0 + v_{xc}(n_0). \tag{86c}$$

Let us now look at what consequences Eqs. (73) and (74) have for the class of ionization models considered in case (a). We conclude that $Z_b(n_0,n(\vec{r}),\{n_s\},\{n_k\})$ should not depend on $\{n_k\}$ since due to Eqs. (80a) and (80b) the first term in Eq. (74) is zero and the second leads to

$$\left.\frac{\delta Z_b(n_0,n(\vec{r}),\{n_s\},\{n_k\})}{\delta n_k}\right|_{n_0,n(\vec{r}),\{n_s\}=\text{const}} = 0. \tag{87}$$

From Eq. (73) we get in case (a),

$$2\left[\varepsilon_s + v_{xc}(n_0) - \gamma + \lambda + T\ln\left(\frac{n_s}{1-n_s}\right)\right] - \gamma\left.\frac{\delta Z_b(n_0,n(\vec{r}),\{n_s\})}{\delta n_s}\right|_{n_0,n(\vec{r})=\text{const}} = 0. \tag{88}$$

Comparing Eq. (88) with Eq. (86a) it is clear that in order to get for the bound states the Fermi-Dirac occupation numbers with the same chemical potential as the Fermi-Dirac occupation numbers of free states one shall have

$$\left.\frac{\delta Z_b(n_0,n(\vec{r}),\{n_s\})}{\delta n_s}\right|_{n_0,n(\vec{r})=\text{const}} = 0. \tag{89a}$$

In such a way we get that in the present case the general dependence of Eq. (56c) is reduced to $Z_b=Z_b(n_0,n(\vec{r}))$ with a linear functional dependence on $n(\vec{r})$. Thus the only physically acceptable ionization model fulfilling the conditions obtained from variational results in the present case is the ionization model given in Eq. (38) [i.e., the ionization model with Z_b from Eq. (85a)]. In the case of Eq. (38) we get

$$n_s = \frac{1}{\exp[\beta(\varepsilon_s - \mu_0) + 1]}. \tag{89b}$$

Case (b). The unphysical term in the potential disappears also when $Z_b(n_0, n(\vec{r}), \{n_s\}, \{n_k\})$ does not depend on $n(\vec{r})$, i.e., when we have

$$Z_b(n_0, n(\vec{r}), \{n_s\}, \{n_k\}) = Z_b[n_0, \{n_s\}, \{n_k\}]. \tag{90}$$

Let us again note that this is the situation if one chooses the ionization model given in Eq. (56b). In the case of the ionization models of Eq. (90) we will get from Eq. (80b),

$$\tilde{\mu}_k = \varepsilon_k + v_{xc}(n_0) + \lambda + T \ln\left(\frac{n_k}{1 - n_k}\right) = 0, \tag{91a}$$

and since Eq. (86b) holds in the present case,

$$-\lambda = \mu_0 + v_{xc}(n_0). \tag{91b}$$

From Eq. (74) we get the same result as in case (a), i.e., Eq. (87). The variation with respect to the occupation numbers of the bound states now provides

$$2\left[\varepsilon_s + v_{xc}(n_0) + \lambda + T \ln\left(\frac{n_s}{1 - n_s}\right)\right] - \gamma \left.\frac{\delta Z_b(n_0, \{n_s\})}{\delta n_s}\right|_{n_0, n(\vec{r}) = \text{const}} = 0. \tag{92}$$

Comparing Eqs. (92) and (89a) one finds that the disappearance of the last term in Eq. (92) is necessary if the bound states have to have the Fermi-Dirac distributions with the same chemical potential as that of the free states. Then, however, one should have in the case considered here,

$$Z_b = Z_b(n_0), \tag{93}$$

that excludes all reasonable ionization models and, in particular, the ionization model proposed in Eq. (56b). Thus the requirement that the chemical potential be the same for bound and free states excludes all the class of ionization models considered in case (b).

D. Results from the variational approach in the QAA case with the ionization model of Eq. (38)

The choice of the ionization model Eq. (38) and the stationarity of Ω_{QAA} with respect to all first-order variables, i.e., all variables except n_0, leads to the first-order occupation numbers for both bound [Eq. (89b)] and free states [Eq. (86b)] in the Fermi-Dirac form with the same chemical potential μ_0 as in the zero-order occupation numbers. The SCF potential $V(\vec{r}) = V_{in}(\vec{r})$, where the interaction potential is given in Eq. (70). Again as in the TF case, the radius $R = R_{WS}$ [see Eq. (39)] due to the neutrality equation and to the ionization model [see two Lagrange terms in Eq. (62)]. The Lagrange multiplier λ is given in Eq. (76) and γ can be found from Eq. (86c) and Eq. (76),

$$\gamma = \mu_0 + v_{xc}(n_0) + e^2 V_{el}(R). \tag{94}$$

It remains now to exploit the last variation equation, namely, the stationarity of Ω_{QAA} with respect to n_0, that involves both the zero- and the first-order contribution to the thermodynamic potential of Eq. (62). Taking into account that $\delta f_0^{(0)}(n_0; T) / \delta n_0 = \mu_0$ [see Sec. IV and Eq. (76)] one gets easily from Eq. (62),

$$\begin{aligned} \left.\frac{\delta \Omega_{QAA}}{\delta n_0}\right|_{V(\vec{r}), \{n_s\}, \{n_k\}} &= \frac{\mu_0 + v_{xc}(n_0) + e^2 V_{el}(R_{WS}) - \gamma}{n_i} \\ &\quad + \int d^3 r [-\mu_0 - v_{xc}(n_0) - e^2 V_{el}(R_{WS}) \\ &\quad + \gamma + \theta(r - R_{WS}) e^2 V_{el}(\vec{r})] \\ &= \int d^3 r\, \theta(r - R_{WS}) e^2 V_{el}(\vec{r}) = 0, \end{aligned} \tag{95}$$

where we have used Eq. (94). We get in Eq. (95) the same relation as in the TF case [compare Eq. (48)] however, now the electrostatic potential $V_{el}(\vec{r})$ is calculated within the SCF QAA scheme. More important—this potential is not equal to zero beyond the WS radius but has an oscillatory behavior there due to the presence of the Friedel terms in the quantum expression for the first-order electronic density. Again as in the TF case, Eq. (95) is the last of the system of the SCF variational equation in the QAA case that should allow one to calculate the average electron density n_0. It would probably be difficult to say at which condition the SCF equations for the quantum average atom in plasma may have a rigorous solution with the left-hand side of Eq. (95) equal to zero. We have only shown that the variational approach to QAA in plasma requires the ionization model of Eq. (38), which in turn leads to the system of equations obtained in this section.

We have seen that in the case of the Thomas-Fermi approximation, Eq. (48) leads to the usual neutrality condition of the Wigner-Seitz sphere that allows one to find the chemical potential. It can be shown that we can rewrite Eq. (95) in the form similar to the usual condition for the chemical potential

$$4\pi \int_0^{R_{WS}} dr\, r^2 n(r) = Z + \Delta Z, \tag{96a}$$

with

$$\Delta Z = 2 R_{WS} V_{el}(R_{WS}) - \frac{4\pi}{R_{WS}^2} \int_R^\infty dr\, r^4 [n(r) - n_0]. \tag{96b}$$

However, from a practical point of view it appears that the calculation of the "correction term" ΔZ is difficult numerically since for large r the r^4 factor could amplify errors in the numerically calculated density difference.

E. Pressure calculation in the quantum average atom in plasma

Again we calculate pressure from the standard thermodynamic definition,

$$P = n_i^2 \left.\frac{\partial F_{QAA}}{\partial n_i}\right|_{T=\mathrm{const}} = n_i^2 \left(\frac{\partial \Omega_{QAA}}{\partial n_i}\right)_{\mathrm{explicit}}. \tag{97}$$

Immediately we get from Eqs. (62) and (94),

$$\begin{aligned} P &= [-f_0(n_0,T) + \gamma n_0]|_{n_0=n_{0,eq},\gamma=\gamma_{eq}} \\ &= \{-f_0^{(0)}(n_0;T) - f_{xc}(n_0) + n_0[\mu_0(n_0;T) + v_{xc}(n_0) \\ &\quad + e^2 V_{el}(R_{WS})]\}|_{n_0=n_{0,eq}}, \end{aligned} \tag{98}$$

where the index "*eq*" means that the corresponding quantity is taken at equilibrium. Again, as in the TF case we get an equation formally similar to the one of an ideal gas except that in Eq. (98) there is a direct contribution of exchange and correlation in the form $f_{xc}(n_{0,eq};T) - n_{0,eq} v_{xc}(n_{0,eq})$. There is also an additional term due to the fact that $V_{el}(R_{WS})$ is, in general, nonzero thus instead of the chemical potential μ_0 appears the electrochemical potential $\mu_0 + e^2 V_{el}(R_{WS})$.

VI. SUPERCONFIGURATIONS IN PLASMAS

We will now consider the superconfigurations in jellium. Superconfigurations have been introduced by Bar-Shalom *et al.* [4]. This approximation allows one to describe statistical properties of bound electron configurations in ground and excited ions. The superconfigurations in the presence of plasma screening have been proposed in Ref. [5] (see also Refs. [6,22]). The main idea of the superconfiguration approximation is to group ions according to their bound-electron occupation numbers of one-electron shells. The superconfigurations contain the so-called supershells, i.e., groups of shells that are close in energy (in terms of the thermal energy equal to T). The total number of bound electrons in each supershell is an integer. In such a way each superconfiguration can represent a large number of ordinary configurations (for details see Refs. [4–6,22]). In our variational approach to superconfigurations in plasma we will use first-order potentials and occupation numbers as variational variables and apply similar methods as in the approach to the QAA case (see Sec. V).

The first-order correction to the free energy will involve all the superconfigurations that are included in the plasma model. As concerns the notations the superconfigurations are numbered by the index Ξ, which defines the structure of its bound electron population. Each superconfiguration is defined by an ensemble of supershells $\{\sigma\} \in \Xi$. We thus have $\{s \in \sigma\}$, where s are ordinary shells.

A. Free energy of superconfigurations in plasmas

The superconfiguration Ξ has $Q_\sigma^{(\Xi)}$ electrons on the supershell σ. There will be the following constraints on the bound shell occupation numbers:

$$2\sum_{s\in\sigma} n_s^{(\Xi)} = Q_\sigma^{(\Xi)}. \tag{99a}$$

The total number of bound electrons of the superconfiguration Ξ is

$$\sum_{\sigma\in\Xi} Q_\sigma^{(\Xi)} = Q_\Xi. \tag{99b}$$

We assume that each superconfiguration Ξ in the plasma is also characterized by a local SCF potential V_Ξ. This potential has bound and free states. We denote the bound and free wave functions of V_Ξ as $\psi_s^{(\Xi)}(\vec{r})$, where $s \in B(\Xi)$, the bound spectrum of Ξ, and $\psi_{\vec{k}}^{(\Xi)}(\vec{r})$, respectively. The bound eigenenergies of Ξ are denoted as $\varepsilon_s^{(\Xi)}$. Each superconfiguration has a cavity the radius of which will depend on the index Ξ. The first-order electron density now depends on Ξ and is locally different from densities of other superconfigurations,

$$n_\Xi(\vec{r}) = 2\sum_{s\in B} n_s^{(\Xi)} |\psi_s^{(\Xi)}(\vec{r})|^2 + \frac{2}{(2\pi)^3}\int d^3k\, n_k^{(\Xi)} |\psi_{\vec{k}}^{\Xi}(\vec{r})|^2. \tag{100}$$

For large r all densities $n_\Xi(\vec{r})$ tend to the same asymptotic value that is equal to the average zero-order density n_0.

The free energy of Ξ is of the form

$$\begin{aligned} &\Delta F_\Xi(n_0,\{n_s^{(\Xi)}, s \in B(\Xi)\},\{n_k^{(\Xi)}, k \in F\}, V_\Xi(\vec{r}), R_\Xi; n_i, T, Z) \\ &\quad = \Delta F_\Xi^{(0)} + \Delta F_{\Xi,el} + \Delta F_{\Xi,xc}, \end{aligned} \tag{101}$$

where

$$\begin{aligned} \Delta F_\Xi^{(0)} &= 2\sum_{s\in B}\left\{ n_s^{(\Xi)} \int d^3r\, \psi_s^{(\Xi)*}(\vec{r})\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 \psi_s^{(\Xi)}(\vec{r})\right] - TS_s\right\} \\ &\quad + \int d^3r \frac{2}{(2\pi)^3}\int d^3k \left[\left(n_{\vec{k}}^{(\Xi)}\left\{\psi_{\vec{k}}^{(\Xi)*}(\vec{r})\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 \psi_{\vec{k}}^{(\Xi)}(\vec{r})\right]\right\}\right.\right. \\ &\quad \left.\left. - TS_{\vec{k}}^{(\Xi)} |\psi_{\vec{k}}^{(\Xi)}(\vec{r})|^2 \right) - f_0^{(0)}(n_0)\right], \end{aligned} \tag{102a}$$

$$\begin{aligned} \Delta F_{\Xi,el} &= \int d^3r \left[[n_\Xi(\vec{r}) - \theta(r - R_\Xi) n_0]\left(-\frac{Ze^2}{r} \right.\right. \\ &\quad \left.\left. + \frac{e^2}{2}\int d^3r' \frac{[n_\Xi(\vec{r}\,') - \theta(r' - R_\Xi) n_0]}{|\vec{r} - \vec{r}\,'|}\right)\right], \end{aligned} \tag{102b}$$

$$\Delta F_{\Xi,xc} = \int d^3\vec{r}\{f_{xc}[n_\Xi(\vec{r})] - f_{xc}(n_0)\}. \tag{102c}$$

The contribution of all superconfigurations to the first-order free energy is given as

$$\begin{aligned} &\Delta F_1(n_0,\{W_\Xi\}\{n_s^{(\Xi)}, s \in B(\Xi)\},\{n_k^{(\Xi)}, k \in F\}, \\ &\quad \{V_\Xi(\vec{r})\},\{R_\Xi\}; n_i, T, Z) = \sum_\Xi W_\Xi[\Delta F_\Xi + T\ln(W_\Xi)], \end{aligned} \tag{103}$$

where W_Ξ is the normalized probability of the superconfiguration Ξ. One has

$$\sum W_\Xi = 1. \tag{104}$$

An entropy term corresponding to the distribution of W_Ξ has been added in Eq. (103) (see, for instance, Ref. [17]).

B. Thermodynamic potential in the case of superconfigurations in plasma

In order that all SCF potentials $V_\Xi(\vec{r})$ be local one has to require for each superconfiguration the neutrality condition

$$Z-\int d^3r[n_\Xi(\vec{r})-n_0]-\frac{4\pi R_\Xi^3 n_0}{3}=0. \tag{105}$$

In the ionization model one generalizes Eq. (38) to the case of superconfigurations,

$$\frac{n_0}{n_i}=Z-\sum_\Xi W_\Xi\int d^3r[n_\Xi(\vec{r})-n_0]. \tag{106a}$$

Let us note, however, that

$$\int d^3r[n_\Xi(\vec{r})-n_0]=\sum_{\sigma\in\Xi}\sum_{s\in\sigma}n_s^{(\Xi)}+\int d^3r(n_{\Xi,\mathrm{free}}(\vec{r})-n_0)$$
$$=Q_\Xi+\int d^3r(n_{\Xi,\mathrm{free}}(\vec{r})-n_0), \tag{106b}$$

with the definition

$$n_{\Xi,\mathrm{free}}(\vec{r})=\frac{2}{(2\pi)^3}\int d^3k\,n_k^{(\Xi)}|\psi_{\vec{k}}^{\Xi}(\vec{r})|^2. \tag{106c}$$

Substituting Eq. (106a) into Eq. (105) one gets immediately

$$n_i=\frac{1}{4\pi\bar{R}^3}, \tag{107}$$

where the average radius is defined as

$$\bar{R}=\left(\sum_\Xi W_\Xi R_\Xi^3\right)^{1/3}. \tag{108}$$

The thermodynamic potential of the first order takes the form

$$\Delta\Omega_1(n_0,\{W_\Xi\},\{n_s^{(\Xi)},s\in B(\Xi)\},\{n_k^{(\Xi)},k\in F\},\{V_\Xi(\vec{r})\},\{R_\Xi\};n_i,T,Z)$$
$$=\sum_\Xi W_\Xi[\Delta F_\Xi+T\ln(W_\Xi)]-B\left(\sum_\Xi W_\Xi-1\right)-\gamma\left(\frac{n_0}{n_i}-Z+\sum W_\Xi\int d^3r[n_\Xi(\vec{r})-n_0]\right)$$
$$-\sum_\Xi\lambda_\Xi\left(Z-\int d^3r[n_\Xi(\vec{r})-n_0]-\frac{4\pi R_\Xi^3 n_0}{3}\right)-\sum_\Xi\sum_{\sigma\in\Xi}\mu_\sigma^{(\Xi)}\left(\sum_{s\in\sigma}n_s^{(\Xi)}-Q_\sigma^{(\Xi)}\right). \tag{109}$$

C. Variational calculation in the superconfiguration case

Again since the zero-order F_0 term depends only on the variable n_0 the SCF equations of the superconfiguration model are to be obtained from the first-order equations

$$\frac{\delta\Delta\Omega_1}{\delta V_\Xi(\vec{r})}=0,\quad\frac{\delta\Delta\Omega_1}{\delta n_s^{(\Xi)}}=0,\quad\frac{\delta\Delta\Omega_1}{\delta n_k^{(\Xi)}}=0,$$
$$\frac{\delta\Delta\Omega_1}{\delta R_\Xi}=0,\quad\frac{\delta\Delta\Omega_1}{\delta W_\Xi}=0, \tag{110}$$

for all Ξ, all $s\in B(\Xi)$, and all k. From Eqs. (105) and (106a) one gets immediately,

$$\frac{n_0}{n_i}=Z-\sum_\Xi W_\Xi\left(Z-\frac{4\pi R_\Xi^3}{3}n_0\right)=\frac{4\pi\bar{R}^3}{3}n_0. \tag{111}$$

The first of Eqs. (110) leads to a result similar to the one in the QAA case,

$$\frac{\delta\Delta\Omega_1}{\delta V_\Xi(\vec{r})}=-2e^4W_\Xi\mathop{(S)}_{a\in B(\Xi),F}\mathop{(S)}_{b\in B(\Xi),F}\left(\frac{n_a^{(\Xi)}-n_b^{(\Xi)}}{\varepsilon_a^{(\Xi)}-\varepsilon_b^{(\Xi)}}\right)\Delta V_{\Xi,ab}\psi_a^{(\Xi)}(\vec{r})$$
$$\times\psi_b^{(\Xi)*}(\vec{r})-2e^2W_\Xi\int\frac{d^3k}{(2\pi)^3}|\psi_{\vec{k}}^{(\Xi)}(\vec{r})|^2\frac{\delta n_k^{(\Xi)}}{\delta\varepsilon_k}\tilde{\mu}_k^{(\Xi)}, \tag{112a}$$

where

$$\tilde{\mu}_k^{(\Xi)}=\varepsilon_k^{(\Xi)}+\nu(n_0)-\gamma+T\ln\left(\frac{n_k^{(\Xi)}}{1-n_k^{(\Xi)}}\right)+\frac{1}{W_\Xi}\lambda_\Xi, \tag{112b}$$

$$\Delta V_\Xi(\vec{r})=V_\Xi(\vec{r})-V_{el,\Xi}(\vec{r})+\frac{1}{e^2}\{v_{xc}[n_\Xi(r)]-v_{xc}(n_0)\}, \tag{112c}$$

and

$$V_{el,\Xi}(\vec{r})=\frac{Z}{r}-\int d^3r'\frac{[n_\Xi(\vec{r}\,')-\theta(r'-R)n_0]}{|\vec{r}-\vec{r}\,'|}.$$

Again as in the QAA case (see Sec. V) the nondiagonal terms lead to

$$\Delta V_{\Xi}(\vec{r}) = 0, \tag{113a}$$

and the diagonal term to

$$\tilde{\mu}_k^{(\Xi)} = 0 \tag{113b}$$

that gives

$$\varepsilon_k + v_{xc}(n_0) - \gamma + \ln\left(\frac{n_k^{(\Xi)}}{1 - n_k^{(\Xi)}}\right) + \frac{\lambda_\Xi}{W_\Xi} = 0, \tag{114a}$$

and

$$n_k^{(\Xi)} = \frac{1}{\exp\left\{\beta\left[\varepsilon_k + \nu_{xc}(n_0) - \gamma + \frac{\lambda_\Xi}{W_\Xi}\right]\right\} + 1}. \tag{114b}$$

From the condition that $n_\Xi(\vec{r})$ should tend for large r to the average electron density n_0 we write

$$n_k^{(\Xi)} = n_k^{(0)} = \frac{1}{\exp[\beta(\varepsilon_k - \mu_0)] + 1}, \tag{114c}$$

and get

$$\mu_0 = \gamma - \nu_{xc}(n_0) - \frac{\lambda_\Xi}{W_\Xi}. \tag{114d}$$

The second equation of Eqs. (110) leads to

$$\frac{\delta \Delta\Omega_1}{\delta n_s^{(\Xi)}} = W_\Xi\left(2\tilde{\mu}_s^{(\Xi)} + 2e^2 \int d^3r |\psi_s^{(\Xi)}(\vec{r})|^2 \Delta V_\Xi(\vec{r})\right) = 0, \tag{115a}$$

with

$$\tilde{\mu}_s^{(\Xi)} = \varepsilon_s^{(\Xi)} + v_{xc}(n_0) - \gamma + \ln\left(\frac{n_s^{(\Xi)}}{1 - n_s^{(\Xi)}}\right) + \frac{\lambda_\Xi}{W_\Xi} - \frac{1}{W_\Xi}\mu_\sigma^{(\Xi)}, \tag{115b}$$

and gives

$$\tilde{\mu}_s^{(\Xi)} = 0. \tag{115c}$$

As in the QAA case with the ionization model Eq. (38) the third equation of Eqs. (110) does not provide any additional result. These equations are fulfilled automatically with the expressions for free-electron occupation numbers that are obtained from the first equation of Eqs. (110) and are displayed in Eqs. (114). The fourth equation of Eqs. (110) leads to

$$\frac{\delta \Delta\Omega_\Xi}{\delta R_\Xi} = -W_\Xi 4\pi R_\Xi^2 n_0 e^2 V_{el,\Xi}(R_\Xi) + \lambda_\Xi 4\pi R_\Xi^2 n_0 = 0, \tag{116a}$$

and gives

$$e^2 V_{el,\Xi}(R_\Xi) = \frac{\lambda_\Xi}{W_\Xi}. \tag{116b}$$

From Eq. (114d) we see that the quantity λ_Ξ / W_Ξ is independent on Ξ. Let us denote

$$e^2 \bar{V}_{el} = \frac{\lambda_\Xi}{W_\Xi}. \tag{116c}$$

In such a way, Eqs. (116b) and (111) allows one, in principle, to determine all R_Ξ from the equation

$$V_{el,\Xi}(R_\Xi) = \bar{V}_{el} \quad \text{for all } \Xi. \tag{116d}$$

From Eqs. (115b) and (114d) we get for the bound occupation numbers,

$$n_s^{(\Xi)} = \frac{1}{\exp\left[\beta\left(\varepsilon_s^{(\Xi)} - \mu_0 - \frac{\mu_\sigma^{(\Xi)}}{W_\Xi}\right)\right] + 1}. \tag{116e}$$

The Lagrange multipliers $\mu_\sigma^{(\Xi)}$ have to be determined from Eq. (99a).

The fifth equation from Eqs. (110) gives

$$\frac{\delta \Delta\Omega_1}{\delta W_\Xi} = \Delta F_\Xi + T \ln W_\Xi + T - B - \gamma\left\{\int d^3r [n_\Xi(\vec{r}) - n_0]\right\} = 0. \tag{117a}$$

It can be transformed introducing a useful notation,

$$\int d^3r [n_\Xi(\vec{r}) - n_0] = Z - \frac{4\pi R_\Xi^3}{3} n_0 = Z - \frac{n_0}{n_i^{(\Xi)}} = Z - Z_\Xi^* \equiv \tilde{Q}_\Xi. \tag{117b}$$

From Eq. (117a) and (117b) one gets

$$W_\Xi = A \exp[-\beta(\Delta F_\Xi - \gamma \tilde{Q}_\Xi)], \tag{117c}$$

where

$$A = \frac{1}{\sum_{\Xi'} \exp[-\beta(\Delta F_{\Xi'} - \gamma \tilde{Q}_{\Xi'})]}, \tag{117d}$$

and

$$\gamma = \mu_0 + v_{xc}(n_0) + e^2 \bar{V}_{el}. \tag{117e}$$

The constant B is equal to

$$B = T\left(1 - \log\left\{\sum_{\Xi'} \exp\left[-\frac{1}{T}(\Delta F_{\Xi'} - \gamma \tilde{Q}_{\Xi'})\right]\right\}\right). \tag{117f}$$

The last variation is that with respect to n_0 and involves both the zero and the first-order terms. The calculation is similar to the one in the QAA case. One shall have $\delta\Omega / \delta n_0 = 0$ that reads

$$\frac{1}{n_i}\frac{\delta}{\delta n_0}[f_0^{(0)}(n_0;T)+f_{xc}(n_0)]+\frac{\delta}{\delta n_0}\Delta\Omega_1(n_0,\{W_\Xi\},\{n_s^{(\Xi)},\; s\in B(\Xi)\},\{n_k^{(\Xi)},k\in F\},\{V_\Xi(\vec{r})\},\{R_\Xi\};n_i,T,Z)=0. \tag{118a}$$

One obtains similarly as in the QAA case [see Eq. (95)]

$$\left.\frac{\delta\Delta F_\Xi}{\delta n_0}\right|_{V_\Xi(\vec{r}),n_s^{(\Xi)},n_k^{(\Xi)}=\text{const}} = \int d^3r\left[\left(\frac{\delta n_\Xi(\vec{r})}{\delta n_0}-1\right)[\mu_0+v_{xc}(n_0)] + \theta(r-R_\Xi)e^2V_{el,\Xi}(\vec{r})\right], \tag{118b}$$

and finally,

$$\begin{aligned}\frac{\delta}{\delta n_0}\Omega &= \frac{\mu_0+v_{xc}}{n_i}+\sum_\Xi W_\Xi\frac{\delta F_\Xi}{\delta n_0}-\gamma\left[\frac{1}{n_i}+\sum_\Xi W_\Xi\int d^3r\left(\frac{\delta n_\Xi(\vec{r})}{\delta n_0}-1\right)\right]-\sum_\Xi\lambda_\Xi\left[-\int d^3r\left(\frac{\delta n_\Xi(\vec{r})}{\delta n_0}-1\right)-\frac{4\pi R_\Xi^3}{3}\right]\\ &= \frac{\mu_0+v_{xc}-\gamma}{n_i}+\frac{\lambda_\Xi}{W_\Xi}\sum_\Xi W_\Xi\frac{4\pi R_\Xi^3}{3}-\sum_\Xi W_\Xi\left[\left(\frac{\delta F_\Xi}{\delta n_0}-\gamma+\frac{\lambda_\Xi}{W_\Xi}\right)\int d^3r\left(\frac{\delta n_\Xi(\vec{r})}{\delta n_0}-1\right)\right]\\ &= \frac{\mu_0+v_{xc}-\gamma+e^2\bar{V}_{el}}{n_i}+\sum_\Xi W_\Xi\left[[\mu_0+v_{xc}(n_0)-\gamma+e^2\bar{V}_{el}]\int d^3r\left(\frac{\delta n_\Xi(\vec{r})}{\delta n_0}-1\right)\right]+\sum_\Xi W_\Xi\int d^3r\,\theta(r-R_\Xi)V_{el,\Xi}(\vec{r})=0.\end{aligned} \tag{118c}$$

Using Eq. (117e) this is reduced to

$$\sum_\Xi W_\Xi\int d^3r\;\theta(r-R_\Xi)V_{el,\Xi}(\vec{r})=0. \tag{118d}$$

Equation (118d) is the last equation of the variational system in the case of superconfigurations. It allows one to find in a self-consistent way the average electron density n_0.

D. Pressure calculation in the superconfiguration case

One uses the standard identity in the superconfiguration case

$$P=n_i^2\left.\frac{\partial F}{\partial n_i}\right|_{T=\text{const}}=n_i^2\left(\frac{\partial\Omega}{\partial n_i}\right)_{\text{explicit}} \tag{119a}$$

that leads immediately to the following expression for the thermodynamic pressure:

$$\begin{aligned}P&=n_i^2\left.\left(-\frac{1}{n_i^2}[f_0^{(0)}(n_0;T)+f_{xc}(n_0)]+\gamma\frac{n_0}{n_i^2}\right)\right|_{n_0=n_{0,eq},\gamma=\gamma_{eq}}\\ &=\{-f_0^{(0)}(n_0;T)-f_{xc}(n_0)+n_0[\mu_0+v_{xc}(n_0)+e^2\bar{V}_{el}]\}|_{n_0=n_{0,eq}}.\end{aligned} \tag{119b}$$

VII. CONCLUSIONS

In this paper we propose a new variational approach to atoms in plasmas. In plasmas that consist of one element atoms having the atomic number Z the equilibrium and all thermodynamic quantities are determined by three parameters: the temperature (T), atom (ion) density (n_i), and Z. In our approach we approximate the functional of the free energy per ion by the first two terms of the cluster expansion with respect to the ion configurations. The zero-order term is the free energy of a homogeneous electron gas (jellium) of unknown density. The first-order term is the correction due to one ion configurations. This correction is constructed according to the scheme of the cluster expansion. It is given by the spatial integral from a difference between two expressions of the plasma free-energy density: the first is the nonhomogeneous free-energy density of the system ion+jellium and the second is the free energy of the homogeneous electron gas (jellium), the same as that which stands in the zero-order expression. The system ion+jellium takes into account the interaction between the central ion and its surrounding plasma. We have considered three approximations to this first-order system: the Thomas-Fermi-atom-in-plasma (TF), the quantum average atom-in-plasma (QAA), and the superconfigurations-in-plasma (SCs). A subtle point in the first-order system is connected to the noncentral ions. These are represented by a constant charge density of the value equal to the zero order (or average) electron charge density but of opposite sign except in a central cavity of unknown radius where their charge density is zero. As concerns the introduction of this cavity we follow the well-known Liberman's Inferno model [9,10]. The cavity concept has also been used in Ref. [12]. In fact the cavity representing noncentral ions corresponds to the simplest possible ion-ion correlation function $g_{ii}(r)\propto\theta(r-R)$, where R is the radius of the cavity and is treated as a variational parameter. It is well known that without a cavity there is no way to have a realistic description of the screened central ion since the charge generated by bound states with the Friedel terms alone cannot screen the nuclear charge Ze. The plasma screening is due to both electrons and ions and cannot be modeled without the noncentral ions. Thus even from the practical point of view the cavity has to be included. As concerns this point it is interesting that our variational approach leads to the following condition on the central ion SCF potential: $\int d^3r\, \theta(r-R)V_{el}(\vec{r})=0$ (or its average in the superconfigurations case). This condition has never been obtained in previous variational approaches [9,10,12]. It allows one, in principle, to determine the average electron density. The variational procedure in our approach in some sense "tries to repair" the default in the cluster expansion due to the presence of the cavity: we get from this procedure that the noncentral ion charge distribution should not interact with the screened SCF electrostatic potential $V_{el}(\vec{r})$ created in the vicinity of the central ion. Our statement concerning "two first terms of the cluster expansion" should be understood in this sense.

The condition allowing one to determine n_0 is the result of the main idea of our variational approach. We minimize the sum of the zero- and the first-order contributions to the free energy per ion while in previous approaches the minimization procedure involved only the first-order contribution to the free energy per ion. In our approach the zero-order term is included and n_0 is treated as a supplementary independent variable along with all other variables describing the central ion structure. In such a way our approach is fully variational: the equilibrium is found from the fact that free energy per ion is stationary with respect to all functions and variables except the parameters T, n_i, and Z. That has not been the case in the mentioned previous approaches in which n_0 is determined from a supplementary nonvariational condition (as the neutrality of the Wigner-Seitz sphere in the Inferno approach). The presence of a supplementary nonvariational condition is the cause that previous approaches are not fully variational. This nonvariational character has its impact on the equation of state. In a nonvariational approach, besides the fact that the procedure does not guarantee that the equilibrium state is correctly constructed, the expression for the electronic pressure also becomes complicated and requires in practice a numerical differentiation. The nonvariational character of the previous approaches is at the origin of the fact that they do not respect the virial theorem.

In our approach the inclusion of the zero-order term depending on an average unknown electron density n_0 requires that we supply the model with a relation between n_0 and the first-order functions and variables describing the central ion. We call this relation the "ionization model." We have checked that the correct ionization model in the case of the Thomas-Fermi expressions for the free energy is the relation $n_0/n_i=Z-\int d^3r[n(\vec{r})-n_0]$, where $n(\vec{r})$ is the total first-order electron density. With this ionization model the TF version of our variational approach leads to SCF equations that appear to be identical with the classical TF ion-in-cell model at the finite temperature first considered in Ref. [1].

In the case of the quantum average atom in plasma and of the superconfigurations in plasma one can, in principle, argue that the ionization model could be different. For instance, the presence of bound states in both these cases makes the following ionization model attractive: $n_0/n_i=Z-2\Sigma_{s\in B}n_s$, where n_s is the occupation of the bound state s. The latter ionization model is not expressed by the first-order electron density but depends only on the occupations of the bound states. The density-functional theory (DFT) is not well suited in such cases. In order to see what consequences may have the choice of an arbitrary ionization model on our variational approach we have proposed a variational procedure that goes beyond the DFT. In this procedure presented in Sec. V in the case of QAA and in Sec. VI in the case of SCs we do not assume that the occupation numbers of the bound and free states have the Fermi-Dirac form but can be arbitrary with their form determined by the variational calculation. The result of the procedure is that the free-electron occupation numbers should always be of the Fermi-Dirac form with the same chemical potential as that connected to the average electron density n_0 of the zero order. As concerns the bound state occupation numbers the choice of the latter ionization model leads to the bound electrons having Fermi-Dirac statistics with chemical potential different from that of the free electrons. That situation which cannot be accepted from the physical point of view holds also in all ionization models that do not depend on the electron density as a whole and treat differently bound and free occupation numbers. We arrive at the conclusion that one shall always choose the ionization model that is a linear functional of the first-order electron density. The ionization model $n_0/n_i=Z-\int d^3r[n(\vec{r})-n_0]$ is not only suitable in the Thomas-Fermi case but one shall apply this model (or its average in the SCs case) in all considered cases, i.e., also in two quantum cases (QAA and SCs) considered in the present paper.

The ionization model is a condition that is to be respected in the variational procedure. It enters the thermodynamic potential with a Lagrange multiplier. Another condition is the locality of the SCF potential that requires the respect of the neutrality condition. In the TF and QAA case this neutrality condition has the form $Z-\int d^3r[n(\vec{r})-n_0]-4\pi R^3n_0/3=0$. In the case of SCs the same condition holds for every SC. The consequence of the ionization model and the neutrality condition is that the radius R (or its average in the SCs case) becomes the Wigner-Seitz radius.

The consequence of the fully variational character of our approach is a simple expression for the thermodynamic pressure that is obtained from the explicit dependence of the thermodynamic potential with respect to the ion density n_i. As obtained first in Ref. [1] in the TF case we get the classical EOS $P=-f_0(n_0(T,n_i,Z))+n_0(T,n_i,Z)\mu_0(T,n_i,Z)$, which is formally identical to that of the ideal quantum electron gas except that the average free electron density (or chemical potential) is to be determined from the TF nonlinear equation. In the QAA and in the SCs cases we get similar simple EOS expressions except that instead of the chemical potential entering the sum $\mu_0+e^2V_{el}(R)$ it is the electrochemical potential at the WS radius, and a correction additionally appears due to the exchange-correlation free energy. In the case of the SCs, instead of μ_0, $\mu_0+e^2\bar{V}_{el}$ enters and appears a similar exchange-correlation contribution. In the latter case there is also an additional requirement that the electrochemical potential at the cavity radius be the same for each SC.

The virial theorem in our model is respected provided the exchange-correlation free energy scales according to the similarity rules established in Ref. [1] (see Sec. II). This is the case with the exchange-correlation free energy from Ref. [16]. However, since the direct EOS expression for the thermodynamic pressure we get is very simple, there is no need to write or use the explicit form of the virial theorem. This explicit form may be complicated due to the fact that the exchange-correlation free energy depends both on the temperature and on the charge square e^2.

In conclusion, we believe that our new approach provides a formally correct solution to a long-standing classical problem in the quantum plasmas: how to find the correct fully variational self-consistent equilibrium of atoms immersed in plasmas in which free electrons are treated quantum mechanically. Our approach allows one to answer practically all questions related to this problem and to better understand previous approaches to the problem. Our next step will be the development of appropriate numerical schemes based on the present theory that will be implemented in numerical codes. The models of the Thomas-Fermi atoms, of the quantum average atom as well as of the detailed configurations or superconfigurations in plasma, are often used in numerical codes for the dense plasma experiments and calculations (see, for instance, Refs. [23–27]); so our theoretical results published here can be interesting for the dense plasma physics community working on an interpretation of laboratory experiments and involved in various dense plasma and astrophysical modelings.

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APPENDIX A: PRESSURE FORMULA FROM FULLY VARIATIONAL FORMULATION

From the variational Eq. (10), and from the definition of the thermodynamic potential Eq. (7), we have at the equilibrium,

$$\frac{\delta F}{\delta X} = \sum_{j=1,J} \lambda_j \frac{\delta C_j}{\delta X}. \qquad \text{(A1)}$$

In the pressure formula Eq. (11), we have to calculate the derivative $\delta/\delta n_i$ of the free energy per ion with respect to the ion density. At the equilibrium the free energy depends only on n_i, T, and Z. The derivative with respect to n_i at a constant temperature and atomic number is thus

$$\left.\frac{\delta F[X_{eq}(n_i,T,Z);n_i,T,Z]}{\delta n_i}\right|_{T,Z}.$$

The total dependence of the free energy with respect to the ion density includes the dependence through the values of all the variables at equilibrium and the explicit dependence of the free-energy functional on the ion density. We thus have

$$\begin{aligned}
\frac{\delta F}{\delta n_i} = & \left.\left[\left(\left.\frac{\delta F}{\delta X}(X;n_i,T,Z)\right|_{X=X_{eq}(n_i,T,Z)}\right)\left(\frac{\delta X_{eq}(n_i,T,Z)}{\delta n_i}\right) + \left(\frac{\delta F}{\delta n_i}(X_{eq};n_i,T,Z)\right)_{\text{explicit}}\right]\right|_{T,Z=\text{const}} \\
= & \left.\left[\sum_j \lambda_j \left(\left.\frac{\delta C_j}{\delta X}(X;n_i,T,Z)\right|_{X=X_{eq}(n_i,T,Z)}\right)\frac{\delta X_{eq}(n_i,T,Z)}{\delta n_i} + \left(\frac{\delta F(X_{eq};n_i,T,Z)}{\delta n_i}\right)_{\text{explicit}}\right]\right|_{T,Z=\text{const}} \\
= & \sum_j \lambda_j \left.\left[\frac{\delta C_j(X_{eq}(n_i,T,Z);n_i,T,Z)}{\delta n_i} - \left(\frac{\delta C_j(X_{eq};n_i,T,Z)}{\delta n_i}\right)_{\text{explicit}}\right]\right|_{T,Z=\text{const}} \\
& + \left.\left(\frac{\delta F(X_{eq};n_i,T,Z)}{\delta n_i}\right)_{\text{explicit}}\right|_{T,Z=\text{const}} \\
= & \left.\left(\frac{\delta \Omega(X_{eq};n_i,T,Z)}{\delta n_i}\right)_{\text{explicit}}\right|_{T,Z=\text{const}}. \qquad \text{(A2)}
\end{aligned}$$

We have used the fact that the total derivative $\delta C_j/\delta n_i|_{T,Z=\text{const}}=0$ since $C_j=0$ throughout the minimization procedure. The last term on the RHS of Eq. (A2) means the derivative with respect to the explicit dependence of the thermodynamic potential on the ion density with all variables taken at their equilibrium values at a constant temperature and atomic number.

APPENDIX B: ON THE EQUIVALENCE OF OUR MODEL IN THE TF CASE AND THE ION-IN-CELL TF MODEL OF REF. [1]

We argue [18] that the variational solution of our model with the TF approximation to ΔF_1 is identical to the solution to the TF ion-in-cell model of Ref. [1]. The solution of our model with the TF approximation for ΔF_1 leads to Eqs. (30), (31), (46), (47b), and (48). Equation (48) is equivalent to a Poisson equation and since the potential and density are spherically symmetric this equation can be written as

$$\frac{1}{r}\frac{d^2}{dr^2}[re^2V(r)] = 4\pi e^2[n(r) - \theta(r-R_{WS})n_0], \qquad \text{(B1)}$$

with the boundary conditions

$$V(r) \underset{r\to 0}{\longrightarrow} \frac{Z}{r} \tag{B2}$$

and

$$V(r) \underset{r\to\infty}{\longrightarrow} 0 \tag{B3}$$

sufficiently fast due to the neutrality condition Eq. (37).

As results from Eqs. (30) and (31), the TF first-order electron density is a nonlinear function of the potential $V(r)$,

$$n(r) = \frac{2}{(2\pi)^3}\int d^3k \frac{1}{\exp\{\beta[\varepsilon_k - e^2V(r) - \mu_0]\} + 1}, \tag{B4}$$

where the chemical potential μ_0 is related to the average zero-order density n_0,

$$n_0 = \frac{2}{(2\pi)^3}\int d^3k \frac{1}{\exp[\beta(\varepsilon_k - \mu_0)] + 1}. \tag{B5}$$

We show in this Appendix that the TF ion-in-cell model of Ref. [1] is identical to our variational solution, as expressed by Eqs. (B1)–(B5) and (48).

We have to show that from Eqs. (B1)–(B5) and (48) it follows that

$$V(r) = 0 \quad \text{for } r \geqslant R_{WS} \tag{B6}$$

and

$$n(r) = n_0 \quad \text{for } r \geqslant R_{WS}, \tag{B7}$$

which leads to the neutrality of the WS sphere.

The demonstration is based on the fact that the nonlinear dependence of $n(r)$ on $V(r)$ is monotonic. In such a way both these functions have extremes at the same values of r. The electrostatic potential is equal to zero at infinity. Let us first suppose that for the region of $R_{WS} < r < \infty$, $V(r)$ has no extreme. In such a case $V(r)$ does not change sign in the whole region outside the WS radius and should be zero in that region in order to fulfill Eq. (48). From the Poisson Eq. (B1) we get in that case $n(r) = n_0$ for $r > R_{WS}$ and the equivalence holds.

Let us now suppose that the potential $V(r)$ has extremes in the region outside the WS radius. The monotonic dependence of $n(r)$ on $V(r)$ implies that the asymptotic behavior of $V(r)$ has the form of a decaying exponential function of r. This can be directly obtained from the linearized version of Eq. (B1). In such a way an eventual ensemble of points $r > R_{WS}$, where both $n(r)$ and $V(r)$ have extremes, is finite. Let us denote this ensemble $\{r_1, r_2, \ldots, r_M\}$, where $r_j > r_i$ if $j > i$ and consider the integral

$$4\pi e^2 \int_{r_M}^{\infty} dr\, r^2[n(r) - \theta(r-R)n_0] = e^2\int_{r_M}^{\infty} dr\, r^2 \frac{1}{r}\frac{d^2}{dr}[re^2V(r)], \tag{B8}$$

where on the RHS the Poisson equation, Eq. (B1), has been used. Integration by parts leads to

$$\begin{aligned} 4\pi e^2 \int_{r_M}^{\infty} dr\, r^2[n(r) - \theta(r-R)n_0] &= e^2 r\frac{d}{dr}[rV(r)]\Big|_{r_M}^{\infty} - \int_{r_M}^{\infty} dr \frac{d}{dr}[rV(r)] \\ &= -r^2e^2\frac{d}{dr}V(r_M) = 0. \end{aligned} \tag{B9}$$

Since $n(r) - \theta(r-R)n_0$ is a monotonic function of r vanishing at infinity, Eq. (B9) implies that

$$n(r) = n_0 \quad \text{for } r \geqslant r_M. \tag{B10}$$

Using Eqs. (B10) and (B3) we find immediately that the solution of Eq. (B1) in the region $r \geqslant r_M$ gives

$$V(r) = 0 \quad \text{for } r \geqslant r_M. \tag{B11}$$

Similar reasoning can be repeated for each of the regions: $]r_p, r_{p+1}]$, $]r_{p+1}, r_{p+2}], \cdots,]r_{M-1}, r_M]$, where r_p denotes the last of the points $\{r_1, r_2, \ldots, r_M\}$ that is larger than the WS radius R_{WS}. Finally, for the region $]R_{WS}, r_p]$ we have from Eq. (48): $\int_{R_{WS}}^{\infty} dr\, r^2V(r) = \int_{R_{WS}}^{r_p} dr\, r^2V(r) = 0$ and, again, since $V(r)$ does not change sign in the last region, it should be there identically zero and, due to Eq. (B1), we have there $n(r) = n_0$.

We get in this way Eqs. (B6) and (B7). These equations lead to the neutrality of the WS sphere. This can be immediately seen, for instance, by the substitution of Eq. (B10) into the ionization model, Eq. (38). We get

$$\begin{aligned} \frac{n_0}{n_i} = \frac{4\pi R^3}{3}n_0 &= Z - \int d^3r[n(\vec{r}) - n_0] \\ &= Z - \int_{r\leqslant R} d^3rn(\vec{r}) + \frac{4\pi R^3}{3}n_0. \end{aligned} \tag{B12}$$

The term involving n_0 disappears on both sides, however, we are left with the usual Thomas-Fermi-cell neutrality equation

$$\int_{r\leqslant R} d^3rn(\vec{r}) = \int_{r\leqslant R} d^3r \frac{2}{(2\pi)^3}\int d^3k \frac{1}{e^{\beta[\varepsilon_k - e^2V(\vec{r}) - \mu_0]} + 1} = Z, \tag{B13}$$

which allows one to find μ_0.

APPENDIX C: DERIVATION OF EQS. (64) AND (67)

The perturbation theory [21] provides the following identity:

$$\begin{aligned} \frac{\delta\psi_a(\vec{r}\,')}{\delta V(\vec{r})} &= e^2\sum_{r\neq s}\frac{\psi_r^*(\vec{r})\psi_a(\vec{r})}{\varepsilon_r - \varepsilon_a}\psi_r(\vec{r}\,') \\ &\quad + \frac{1}{(2\pi)^3}e^2\int d^3k' \frac{\psi_{\vec{k}'}^*(\vec{r})\psi_a(\vec{r})}{\varepsilon_{\vec{k}'} - \varepsilon_a}\psi_{\vec{k}'}(\vec{r}\,'), \end{aligned} \tag{C1}$$

with $a = s$ or $a = \vec{k}$; and $\psi_s(\vec{r})$ and $\psi_{\vec{k}}(\vec{r})$ being bound and free wave functions, respectively, solutions to the Schrödinger equations with the potential $-e^2V(\vec{r})$. We note that the bound contribution of the noninteraction part of the free energy is of the following form with S_s independent on the potential $V(\vec{r})$:

$$\Delta F_{1,0}^{(b)} = 2\sum_{s\in B}\left[n_s\int d^3r\,\psi_s^*(\vec r)\left(-\frac{\hbar^2}{2m}\vec\nabla^2\psi_s(\vec r)\right) - TS_s\right]$$

using Eq. (C1) and the Schrödinger equation, Eq. (57), we get

$$\begin{aligned}\frac{\delta\Delta F_{1,0}^{(b)}}{\delta V(\vec r)} &= 2e^4\sum_{s\neq r} n_s\left(\frac{\psi_r(\vec r)\psi_s^*(\vec r)}{\varepsilon_r-\varepsilon_s}V_{rs} + \frac{\psi_r^*(\vec r)\psi_s(\vec r)}{\varepsilon_r-\varepsilon_s}V_{rs}^*\right)\\ &\quad + 2e^4\int\frac{d^3k'}{(2\pi)^3}\sum_s n_s\left(\frac{\psi_{\vec k'}(\vec r)\psi_s^*(\vec r)}{\varepsilon_{k'}-\varepsilon_s}V_{\vec k' s}\right.\\ &\quad \left. + \frac{\psi^*_{\vec k'}(\vec r)\psi_s(\vec r)}{\varepsilon_{k'}-\varepsilon_s}V^*_{\vec k' s}\right). \end{aligned}\tag{C2a}$$

Changing the names of the integration variables we can write Eq. (C2a) in a more compact form,

$$\frac{\delta\Delta F_{1,0}^{(b)}}{\delta V(\vec r)} = -2e^4\sum_{s\neq r}\frac{n_s-n_r}{\varepsilon_s-\varepsilon_r}\psi_r(\vec r)\psi_s^*(\vec r)V_{rs}. \tag{C2b}$$

Similarly, we get for the free electron part of the noninteracting free energy,

$$\begin{aligned}\Delta F_{1,0}^{(f)} &= 2\int\frac{d^3k}{(2\pi)^3}\int d^3r\left\{\psi^*_{\vec k}(\vec r)\left[n_k\left(-\frac{\hbar^2}{2m}\vec\nabla^2\psi_{\vec k}(\vec r)\right)\right.\right.\\ &\quad \left.\left. - TS_k\psi_{\vec k}(\vec r)\right] - f_0^{(0)}\right\},\end{aligned}\tag{C3}$$

where now the entropy term is multiplied by the free particle term $|\psi_{\vec k}^{(\vec r)}|^2$. As said before the convergence of the space integral in Eq. (C3) is guaranteed by Eqs. (58a) and (58b). We get

$$\begin{aligned}\frac{\delta\Delta F^{(f)}_{1,0}}{\delta V(\vec r)} &= -2e^4\sum_r\int\frac{d^3k}{(2\pi)^3}\left(\frac{n_k-n_r}{\varepsilon_k-\varepsilon_r}\right)\psi_r(\vec r)\psi^*_{\vec k}(\vec r)V_{r\vec k}\\ &\quad - 2e^4\int\frac{d^3k'}{(2\pi)^3}\int\frac{d^3k}{(2\pi)^3}\left(\frac{n_k-n_{k'}}{\varepsilon_k-\varepsilon_{k'}}\right)\psi_{\vec k'}(\vec r)\psi^*_{\vec k}(\vec r)V_{\vec k'\vec k}\\ &\quad - 2e^2\int\frac{d^3k'}{(2\pi)^3}\int\frac{d^3k}{(2\pi)^3}\psi_{\vec k'}(\vec r)\psi^*_{\vec k}(\vec r)(2\pi)^3\delta(\vec k-\vec k')\\ &\quad \times\left[\varepsilon_k\left(\frac{n_k-n_{k'}}{\varepsilon_k-\varepsilon_{k'}}\right) - T\left(\frac{S_k-S_{k'}}{\varepsilon_k-\varepsilon_{k'}}\right)\right].\end{aligned}\tag{C4}$$

Summing up the above results we write

$$\frac{\delta\Delta F_{1,0}}{\delta V(\vec r)} = \left(\frac{\delta\Delta F_{1,0}}{\delta V(\vec r)}\right)_1 + \left(\frac{\delta\Delta F_{1,0}}{\delta V(\vec r)}\right)_2, \tag{C5}$$

where

$$\left(\frac{\delta F_{1,0}}{\delta V(\vec r)}\right)_1 = -2e^4 \mathop{(S)}_{a\in B,F}\ \mathop{(S)}_{b\in B,F}\left(\frac{n_a-n_b}{\varepsilon_a-\varepsilon_b}\right)V_{ab}\psi_a(\vec r)\psi_b^*(\vec r), \tag{C6}$$

$$\begin{aligned}\left(\frac{\delta F_{1,0}}{\delta V(\vec r)}\right)_2 &= -2e^2\int_0^\infty\frac{dk}{(2\pi)^3}\int_0^\infty dk'\,k'^2\frac{\delta(k-k')}{k'^2}\\ &\quad \times\left[\varepsilon_k\left(\frac{n_k-n_{k'}}{\varepsilon_k-\varepsilon_{k'}}\right)-T\left(\frac{S_k-S_{k'}}{\varepsilon_k-\varepsilon_{k'}}\right)\right]\int d\hat\Omega_{\vec k}\int d\hat\Omega_{\vec k'}\\ &\quad \times\delta(\hat\Omega_{\vec k}-\hat\Omega_{\vec k'})\psi_{\vec k'}(\vec r)\psi^*_{\vec k}(\vec r).\end{aligned}\tag{C7}$$

Using $\varepsilon_k-\varepsilon_{k'}=(\hbar^2/2m)(k-k')(k+k')$, $(m/\hbar^2)(1/k)(\delta/\delta k)=\delta/\delta\varepsilon_k$ and the identity $-T\delta S_k/\delta\varepsilon_k=(\delta n_k/\delta\varepsilon_k)\ln[n_k/(1-n_k)]$, we transform Eq. (C7) as follows:

$$\left(\frac{\delta F_{1,0}}{\delta V(\vec r)}\right)_2 = -2e^2\int_0^\infty\frac{dk}{(2\pi)^3}|\psi_{\vec k}(\vec r)|^2\frac{\delta n_k}{\delta\varepsilon_k}\left[\varepsilon_k+\ln\left(\frac{n_k}{1-n_k}\right)\right]. \tag{C8}$$

We have also to calculate

$$\begin{aligned}\frac{\delta(F_{1,1}+F_{1,xc})}{\delta V(\vec r)} &= -\int d^3r'[e^2V_{el}(\vec r') - \{v_{xc}[n(\vec r')]\\ &\quad - v_{xc}(n_0)\}]\frac{\delta n(\vec r')}{\delta V(\vec r)} + v_{xc}(n_0)\int d^3r'\frac{\delta n(\vec r')}{\delta V(\vec r)}\\ &= -\int d^3r'[e^2V(\vec r')-v_{xc}(n_0)]\frac{\delta n(\vec r')}{\delta V(\vec r)},\end{aligned}\tag{C9}$$

and the terms coming from the general form of the ionization, model, Eq. (56c),

$$\begin{aligned}\frac{\delta Z_b(n_0,n(\vec r),\{n_s\},\{n_k\})}{\delta V(\vec r)} &= \int d^3r'\left[\frac{\delta Z_b(n_0,n(\vec r),\{n_s\},\{n_k\})}{\delta n(\vec r')} - \left.\frac{\delta Z_b(n_0,n(\vec r),\{n_s\},\{n_k\})}{\delta n(\vec r')}\right|_{n(\vec r')=n_0}\right]\frac{\delta n(\vec r')}{\delta V(\vec r)}\\ &\quad + \left.\frac{\delta Z_b(n_0,n(\vec r),\{n_s\},\{n_k\})}{\delta n(\vec r')}\right|_{n(\vec r')=n_0}\int d^3r'\frac{\delta n(\vec r')}{\delta V(\vec r)}\\ &= \int d^3r'\{H_{Z_b}[n(r')] - H_{Z_b}(n_0)\}\frac{\delta n(\vec r')}{\delta V(\vec r)} + H_{Z_b}(n_0)\int d^3r'\frac{\delta n(\vec r')}{\delta V(\vec r)}.\end{aligned}\tag{C10}$$

In such a way when calculating the variation of terms other than $\delta F^{(0)}_{1,QAA}/\delta V(\vec r)$ in $\delta\Omega_{QAA}/\delta V(\vec r)$ along the lines as in Eqs. (C2)–(C8) we can treat together the term

$$\int d^3r'[V(\vec{r}\,') - \gamma\{H_{Z_b}[n(\vec{r}\,')] - H_{Z_b}(n_0)\} - v_{xc}(n_0) - \gamma H_{Z_b}(n_0)]\frac{\delta n(\vec{r}\,')}{\delta V(\vec{r})}. \tag{C11}$$

The operator in the integral of Eq. (C11) is Hermitian and the RHS of Eq. (C11) is similar to the kinetic energy and entropy term from Eqs. (C5)–(C7). In such a way we can repeat in Eq. (C11) all the steps used in the derivation of Eqs. (C5)–(C7) and obtain finally Eq. (65).

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